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A Model of Adsorbent Behavior Applied to the Use of Layered Beds in Cycling Zone Adsorption

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Abstract

A simple model of adsorbent behavior in cycling zone adsorption is developed. The model is used to illustrate trends in adsorbent behavior and to investigate the use of layered beds in cycling zone adsorption.

INTRODUCTION

Cycling zone adsorption was first invented by Pigford (*1*) with more recent development done by Wankat (*2*) among others. In the direct-wave mode of operation, a series of adsorbent beds is heated and cooled by external sources as feed continuously enters the first bed. Adjacent beds are cycled out of phase with each other. The separation achieved in a single bed is amplified through the use of succeeding beds. Alternating pulses of two product streams are produced from the final bed.

This process has most commonly been applied to systems where each component in solution is adsorbed independently. Cycling zone adsorption has also been applied in cases where exchange adsorption occurs (*3*). Examples of exchange adsorption are liquid-phase adsorption from concentrated solutions and ion exchange. In both of these cases, one component is adsorbed by displacing another component. The following discussion will be limited to the case of liquid-phase adsorption from concentrated binary solutions in a cycling zone adsorption system operating in the direct-wave mode.

MODEL OF ADSORBENT BEHAVIOR

Consider a solid adsorbent with an interparticle void fraction α, an intraparticle void fraction β, and with a volume of adsorbed solution per volume of bed equal to $\Phi\beta(1-\alpha)$. Material residing within the adsorbent pores but not part of the adsorbed phase is assumed to have the same composition as the bulk solution. Assuming no axial dispersion, a material balance for Component 1 in a binary mixture is given by

$$\left(\frac{\partial}{\partial t}((\alpha+(1-\alpha)\beta(1-\Phi))X_1)\right)_z+\left(\frac{\partial}{\partial t}[(1-\alpha)\beta\Phi\bar{X}_1]\right)_z+\alpha v\left(\frac{\partial X_1}{\partial z}\right)_t=0 \tag{1}$$

Using the product rule and assuming α and β are constant yields

$$[\alpha+(1-\alpha)\beta(1-\Phi)]\left(\frac{\partial X_1}{\partial t}\right)_z+(\bar{X}_1-X_1)(1-\alpha)\beta\left(\frac{\partial\Phi}{\partial t}\right)_z$$
$$+(1-\alpha)\beta\Phi\left(\frac{\partial\bar{X}_1}{\partial t}\right)_z+\alpha v\left(\frac{\partial X_1}{\partial z}\right)_t=0 \tag{2}$$

Assuming local equilibrium, the chain rule yields

$$\left(\frac{\partial\bar{X}_1}{\partial t}\right)_z=\left(\frac{\partial\bar{X}_1}{\partial X_1}\right)_T\left(\frac{\partial X_1}{\partial t}\right)_z+\left(\frac{\partial\bar{X}_1}{\partial T}\right)_{X_1}\left(\frac{\partial T}{\partial t}\right)_z \tag{3}$$

Substituting Eq. (3) into Eq. (2) and multiplying the resulting equation by $(\partial t/\partial T)_z$ yields

$$\left[\alpha+(1-\alpha)\beta(1-\Phi)+(1-\alpha)\beta\Phi\left(\frac{\partial\bar{X}_1}{\partial X_1}\right)_T\right]\left(\frac{\partial X_1}{\partial T}\right)_z$$
$$=-(1-\alpha)\beta\Phi\left(\frac{\partial\bar{X}_1}{\partial T}\right)_{X_1}-(1-\alpha)\beta\left(\frac{\partial\Phi}{\partial T}\right)_z(\bar{X}_1-X_1)$$
$$-\alpha v\left(\frac{\partial X_1}{\partial z}\right)_t\left(\frac{\partial t}{\partial T}\right)_z \tag{4}$$

If it is now assumed that Φ is a function of temperature only and that the temperature change is sufficiently fast so that the term $\alpha v(\partial X_1/\partial z)_t\,(\partial t/\partial T)_z$

is small compared to the other terms in the equation, Eq. (4) can be reduced to

$$\left(\frac{\partial X_1}{\partial T}\right)_z = -\frac{A\left(\frac{\partial \bar{X}_1}{\partial T}\right)_{X_1} + A\frac{d\ln\Phi}{dT}(\bar{X}_1 - X_1)}{1 + A\left(\frac{\partial \bar{X}}{\partial X_1}\right)_T} = P_1 \tag{5}$$

where

$$A = \frac{(1-\alpha)\beta\Phi}{[\alpha + (1-\alpha)\beta(1-\Phi)]} \tag{6}$$

and where the symbol P_1 has been introduced to stand for the quantity $(\partial X_1/\partial T)_z$ with all the assumptions implicit in Eq. (5). P_1 defined in this manner is numerically equal to the quantity $(P/\Delta T)$ used by Rieke (*3*). The quantity A is the ratio of adsorbed-phase volume to bulk-solution volume. Equation (5) could also be derived from Eq. (4) by restricting these equations to the plateau region of a composition profile where $(\partial X_1/\partial z)_t = 0$. The composition change caused by a temperature change for the direct-wave mode of operation is given by

$$\Delta X_1 = \bar{P}_1 \Delta T \tag{7}$$

where $\bar{P}_1$ is the effective average value of P_1 for the step change in temperature.

For an ideal binary system as described by Everett (4), the relative adsorptivity is given by

$$r_{12} = \exp - \left(\frac{\Delta U_1^0 - \Delta U_2^0}{RT} - \frac{\Delta S_1^0 - \Delta S_2^0}{R}\right) = \frac{\bar{Y}_1(1 - Y_1)}{Y_1(1 - \bar{Y}_1)} \tag{8}$$

In general, it is not possible to unambiguously define values for r_{12} and Φ since any determination of r_{12} carries with it an assumption concerning the boundary between the adsorbed phase and the bulk solution (*5, 6*). In most cases it is possible to select a value of Φ such that r_{12} is constant over most of the composition range (*7*). This value for Φ will in general be identifiable with a completely filled monolayer at the adsorbent surface (*6*). It is therefore reasonable to assume that Φ chosen in this manner will be relatively independent of temperature and that the second term in the numerator in Eq. (5) will be small compared to the first term.

By analogy with heat-entropy relationships observed in other phase equilibria, it is likely that the thermal entropies of molecules adsorbed at an interface will be approximately related to the energies of adsorption according to the equations (*4*)

$$\begin{aligned} \Delta S_1^0 &= C + \left(\frac{B}{T}\right)\Delta U_1^0 \\ \Delta S_2^0 &= C + \left(\frac{B}{T}\right)\Delta U_2^0 \end{aligned} \tag{9}$$

where for liquid-phase adsorption (*4*)

$$B \simeq .375 \tag{10}$$

If, in addition, the molar volumes of the components are taken to be constant and unaffected by adsorption, then volume fractions can replace the mole fractions in Eq. (8), and Eqs. (5), (6), (8), (9), and (10) yield

$$P_1 \simeq 1.6\left[\frac{Ar_{12}\ \ln r_{12}\ X_1(1-X_1)}{T[(1+(r_{12}-1)X_1)^2 + Ar_{12}]}\right] \tag{11}$$

$\bar{P}_1$ can be approximated by substituting the average value for the relative adsorptivity ($\bar{r}_{12}$) and temperature ($\bar{T}$) for the step change into Eq. (11). From Eqs. (8) through (10) it follows that

$$\bar{r}_{12} = \frac{r_{12,L} + r_{12,H}}{2} \simeq \frac{1}{2}\left(r_{12,L} + \exp\left(\left(\frac{T_L}{T_H}\right)^{.625} \ln r_{12,L}\right)\right) \tag{12}$$

This analysis can no doubt be made more complicated. However, in their present form, the validity of Eqs. (11) and (12) can be tested using data obtained by Rieke (*3*) for the reasonably ideal system of toluene–heptane adsorption on silica gel. By trial and error, a value for Φ was determined which yields a constant value for $r_{12,L}$ at 2°C. These two quantities along with Rieke's values for α and β were substituted into Eqs. (11) and (12) and the resulting value for P_1 was plotted in Fig. 1 along with experimental values from Rieke (*3*). The agreement appears to be reasonably good. Equilibrium relations from Rieke's data, along with the model parameters, are summarized in Table 1. Rieke's method for measuring adsorbed-phase compositions assumes $\Phi = 1$.

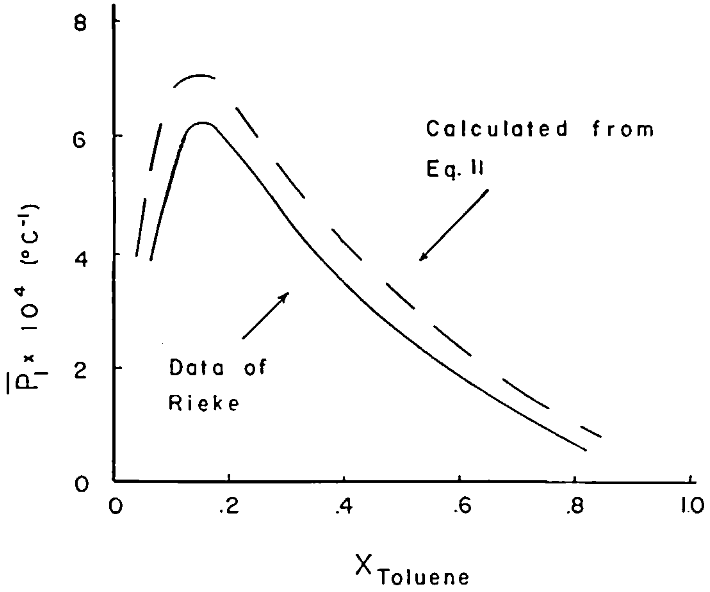

FIG. 1. $\bar{P}_1$ as a function of $\bar{X}_1$ for adsorption on silica gel from a toluene-heptane mixture.

GENERAL TRENDS IN ADSORBENT BEHAVIOR

Because of the numerous assumptions used to derive Eqs. (11) and (12), it is unlikely that these equations could be used to accurately predict the performance of an adsorbent. However, it is reasonable to assume that they can be used to illustrate trends in adsorbent performance. Larger values of $\bar{P}_1$ yield larger composition changes for a given temperature change. It is therefore apparent that the greater the values of $\bar{P}_1$ for a particular adsorbent, the better that adsorbent is for separating a binary mixture. A parameter

TABLE 1
Data for the Adsorption from Toluene-Heptane Solutions on Silica Gel

Rieke data	Model parameters
$\alpha = .403$	$\alpha = .403$
$\beta = .383$	$\beta = .383$
$r_{12,L} = 13.9 \exp(-.99X_1)$	$\Phi = .875$
$r_{12,H} = 8.1 \exp(-.50X_1)$	$r_{12,L} = 17$

which would seem to give a good indication of the effectiveness of an adsorbent used for separations over a large composition range is the integral of P_1 between the limits $X_1 = 0$ and $X_1 = 1$. A plot of this integral as a function of r_{12} for various values of A at a fixed temperature is shown in Fig. 2. At small values of r_{12}, the relative adsorptivity appears to be the largest factor in determining the adsorbent effectiveness. In contrast, at larger values of r_{12}, the parameter A appears to determine the adsorbent effectiveness.

LAYERED-BED CYCLING ZONE ADSORPTION: GENERAL CONSIDERATIONS

In the remainder of this article, a novel cycling zone adsorption technique will be described. Consider a cycling zone adsorption system consisting of a single bed in the direct-wave mode of operation where the bed is composed of layers of adsorbing material chosen so that if the liquid phase is enriched in a component by a temperature increase in one layer, it also would be enriched in that component by a temperature decrease in a succeeding layer. From Eq. (8) it is apparent that this is accomplished if the value of r_{12} increases with temperature in one layer and decreases with temperature in adjacent layers. In general, the value of r_{12} for an adsorbent changes toward the value of 1 as the temperature is increased. It is therefore likely that this type of

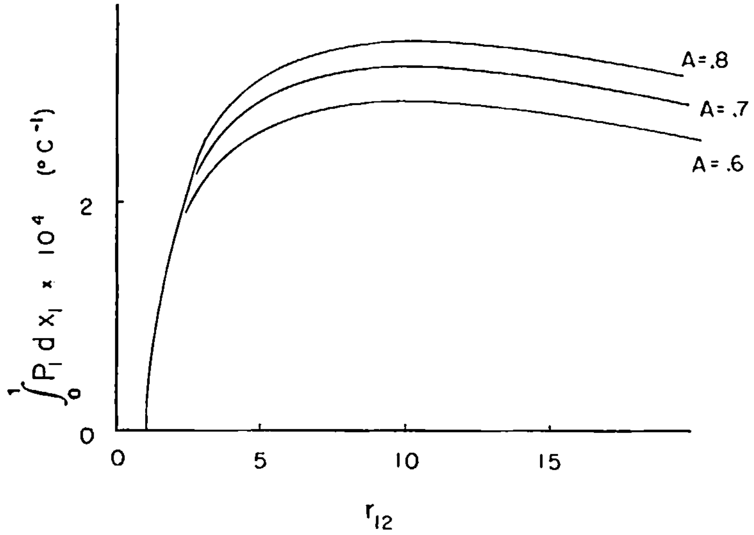

FIG. 2. $\int_0^1 P_1 \, dX_1$ as a function of r_{12} for various values of A.

system could be constructed using an adsorbent bed composed of two adsorbents chosen so that if $r_{12} > 1$ in one layer, then $r_{12} < 1$ in adjacent layers. This is perhaps easiest to visualize using Eqs. (7) and (11) since the value of $\bar{P}_1$ from Eq. (11) would have opposite signs for these two adsorbents. As shown below, in a system constructed in this manner, the separation attained in the first layer could be amplified by the succeeding layers even though the temperatures of all the layers are cycled in phase.

There are at least two examples of pairs of adsorbents and binary mixtures where this condition is satisfied. Silica gel in general selectively adsorbs the aromatic component in an aromatic–aliphatic mixture while data given by Eberly (*8*) indicates that the hydrogen form of alumina-deficient mordentite selectively adsorbs the aliphatic component in such a mixture. In addition, data given by Dernini (*9*) indicates that *p*-xylene is selectively adsorbed from a solution of *p*-xylene and *m*-xylene by barium-substituted type Y zeolite while data given by Eberly (*10*) indicates that the opposite takes place on the calcium form of type 13 A molecular sieve. In all of these examples, the adsorbent pore size is large compared to the size of the adsorbate so that the sieving properties of these adsorbents are not being used.

PERFORMANCE OF A LAYERED-BED CYCLING ZONE ADSORPTION SYSTEM

The performance of a layered bed in the direct-wave mode of operation can be illustrated by the use of an equilibrium model of adsorption. Assuming one-dimensional flow, no axial dispersion, and local equilibrium, a material balance in a region of constant temperature yields

$$(\alpha + (1-\alpha)\beta(1-\Phi))\left(\frac{\partial X_1}{\partial t}\right)_z + (1-\alpha)\beta\Phi\left(\frac{\partial \bar{X}_1}{\partial t}\right)_z + \alpha v\left(\frac{\partial X_1}{\partial z}\right)_t = 0 \tag{13}$$

Equation (13), along with the appropriate boundary conditions and an equilibrium expression relating $\bar{X}_1$ to X_1, has the property that X_1 is constant along characteristic curves given by

$$\frac{dz}{dt} = \frac{v}{1 + \left(\dfrac{\partial \bar{X}_1}{\partial X_1}\right)_T A} = U_c \tag{14}$$

U_c is therefore the velocity at which a concentration wave travels through a bed. Analogously, the velocity of a concentration discontinuity is given by

$$U_c = \frac{v}{1 + \left[\dfrac{\bar{X}_1'' - \bar{X}_1'}{X_1'' - X_1'} \right] A} \tag{15}$$

where the primed quantities denote values on either side of the composition change. The liquid-phase composition remains constant along a characteristic until a temperature change takes place. When the temperature changes, the new composition can be calculated from the simultaneous solution of equilibrium and material-balance relations as described by Rieke (*3*). In the absence of knowledge concerning the temperature dependence of the equilibrium relations, the composition change caused by a temperature change can be approximated by using Eqs. (7), (11), and (12).

Figure 3 illustrates a cycling zone adsorption system consisting of four layers of adsorbent material in a single thermal zone. Adsorbent properties used in subsequent calculations are listed in Table 2. The values for $\bar{r}_{12}$ and A given in this table are representative of the values observed for the adsorbents in the xylene separation example cited above. Other parameters needed in the calculation of the performance of this system are also given in the table.

There are two types of product recycle streams illustrated in Fig. 3. Diffuse composition waves from the effluent are recycled to the inlet of the column by recycle stream 1. This material is assumed to have an average composition equal to that of the feed. In addition, a portion of the product is

TABLE 2
Parameters Used in Layered-Bed Cycling Zone Adsorption Calculation

	Properties of Adsorbents	
	Adsorbent 1	Adsorbent 2
A	.8	.8
$\bar{r}_{12}$	5	.2
	Operating Conditions	
	$\Delta T = 55$ K	
	$X_{1,F} = 0.5$	
	$\dfrac{\text{Flow of recycle stream 2}}{\text{Flow of feed}} = 1.26$	
	$\bar{T} = 325$ K	

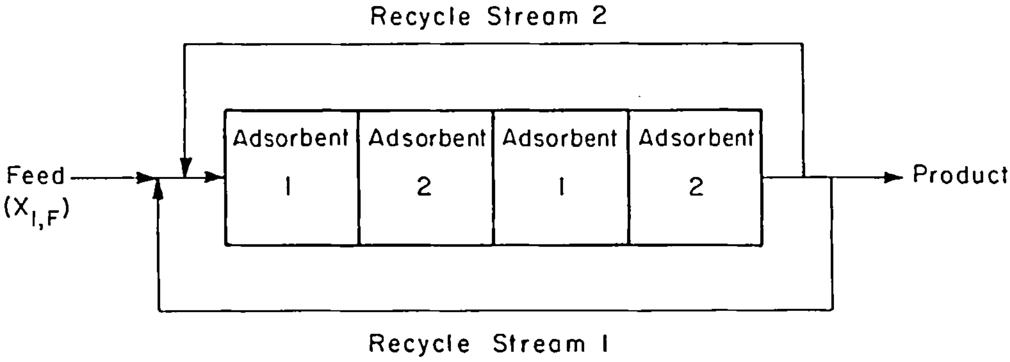

FIG. 3. Layered-bed cycling zone adsorption system with recycle.

recycled back to the column inlet by recycle stream 2 and mixed with the feed stream. This has the effect of producing two pulses of material, one with $X_1 = .6$ and one with $X_1 = .4$, flowing into the first layer of the bed. Details of calculations using recycle in cycling zone adsorption are described by Rieke (*3*).

Calculation results are given in Table 3 and Figs. 4 and 5. In Fig. 4, characteristics from Eqs. (14) and (15) are plotted on a graph of z versus t for five temperature changes. Composition changes were calculated from Eqs. (7), (11), and (12). Composition shock waves are shown as heavy solid lines in the figure. Of particular interest is the observation that since the criteria for diffuse-wave formation is reversed for the two adsorbents, shock waves are formed from simple waves and vice versa from layer to layer. Calculations concerning the formation of shock waves from diffuse waves are described by Vermeulen (*11*). In practice, this behavior could be of considerable utility

TABLE 3
Calculation Results

X_1 of Product 1 = 0.74
X_1 of Product 2 = 0.26

$$\frac{\text{Flow of recycle stream 1}}{\text{Flow of feed}} = 0.76$$

$$\frac{v}{(\text{cycling frequency})\ (\text{bed length})} = 0.74$$

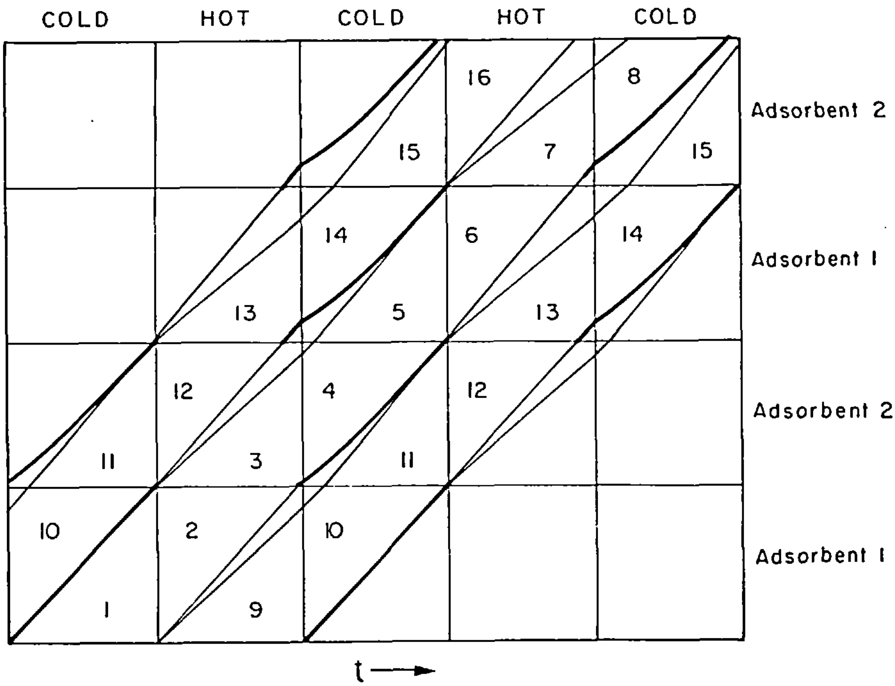

Fig. 4. Method of characteristics solution for layered-bed cycling zone adsorption.

since, in general, the uncontrolled growth of diffuse waves adversely affects the separation attainable in cycling zone adsorption.

Figure 5 illustrates compositions inside the adsorption column for the conditions in Table 2 and Fig. 4. Equilibrium relations for the two adsorbents at the two temperatures of operation are determined from Eq. (12) and plotted in the figure. The progress of the separation can be followed by moving from equilibrium line to equilibrium line in one of two different ways. When the column temperature is changed, the new composition is found by moving from the adsorbent isotherm at the original temperature to the isotherm at the final temperature with a slope of $-A^{-1}$. When moving from one adsorbent layer to the next without changing temperature, the liquid-phase composition does not change while the new adsorbed-phase composition can be found by moving vertically to the next adsorbent's isotherm at the prevailing temperature. The numbers shown in Fig. 5 at these various positions correspond to the same numbers shown in Fig. 4.

In addition to the control over the growth of simple waves, there are at least two other advantages for the use of layered beds in cycling zone

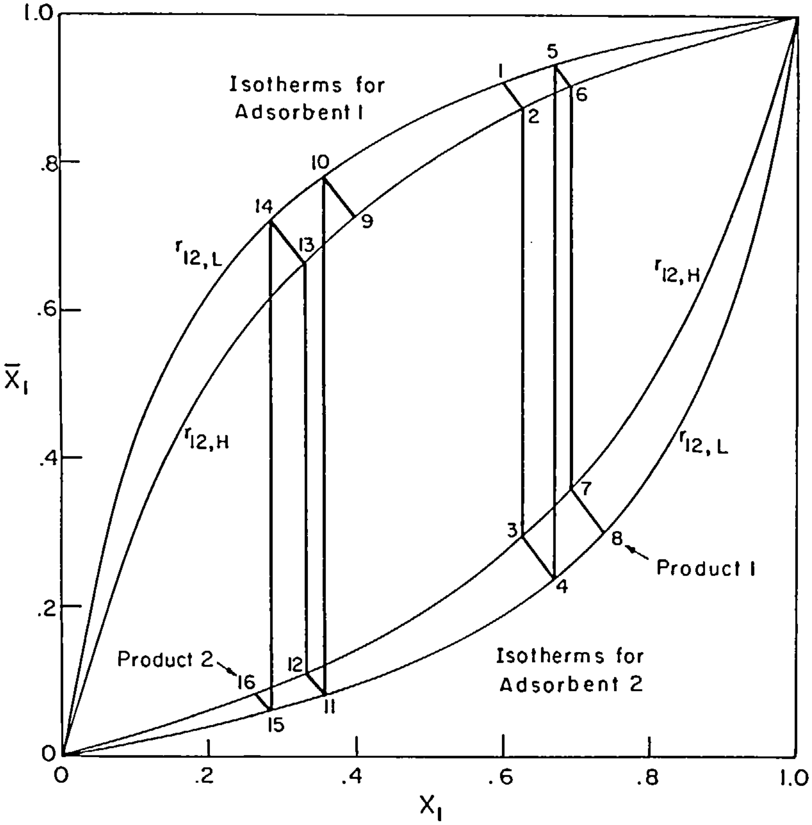

FIG. 5. Equilibrium and material-balance relations in layered-bed cycling zone adsorption.

adsorption. Because a layered-bed cycling zone adsorption system consists of a single thermal zone, it would appear to be simpler to construct than the equivalent multiple-thermal-zone system. Also, since the fluid does not change temperature between layers in the layered-bed design, in operation there should be a closer approach to ideal square-wave cycling as compared to conventional cycling zone adsorption.

SYMBOLS

A	$\{(1-\alpha)\beta\Phi\}/\{\alpha+(1-\alpha)\beta(1-\Phi)\}$
B	constant in Eq. (9)

C	constant in Eq. (9), (cal gmol^{-1} °K^{-1})
P_1	parameter in Eq. (11), (°K^{-1})
$\bar{P}_1$	P_1 corresponding to $\bar{r}_{12}$ and $\bar{T}$ (°K^{-1})
R	gas constant (cal gmol^{-1} °K^{-1})
r_{12}	relative adsorptivity of Component 1 with respect to Component 2
$\bar{r}_{12}$	average value of r_{12} during a temperature change
S	thermal entropy (cal gmol^{-1} °K^{-1})
t	time (s)
T	temperature (°K)
$\bar{T}$	average value of T during a temperature change (°K)
U	internal energy (cal/gmol)
U_c	concentration velocity (cm/s)
v	interstitial velocity (cm/s)
X	volume fraction of a component in the liquid phase
$\bar{X}$	volume fraction of a component in the adsorbed phase
Y	mole fraction of a component in the liquid phase
$\bar{Y}$	mole fraction of a component in the adsorbed phase
z	distance (cm)

Greek Letters

α	interparticle void fraction
β	intraparticle void fraction
Δ	difference operator
Φ	volume fraction of pore occupied by adsorbed solution

Superscripts

$^\circ$	standard state
$'$, $''$	before, after shock front

Subscripts

f	final value
F	feed
H	high temperature
i	initial value

L	low temperature
1, 2	Components 1 and 2

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