Effect of Surface Barrier on the Sorption of Gases in Microporous Solids

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Adsorption rate of gases in microporous solids exhibiting a bimodal pore size distribution depends on the interplay of various processes occurring within the particle. The micropore diffusion, the macropore diffusion, and the surface barrier processes (Fu et al., 1986) could all play a significant role in the global uptake.

Hattori and Murakami (1974), in their adsorption study of benzene on HY and CaY zeolites, have found that a surface mass action model describes their experimental results well.

Past work on bimodal solids have ignored the presence of the surface barrier. Ruckenstein et al. (1971) assumed pore diffusion mechanisms in both macropore and micropore and allowed for adsorptive capacity in both pores. Researchers in the area of zeolite and activated carbon have proposed a different bimodal diffusion model. The essential features of this model are: no adsorption in the macropore, pore diffusion in macropore, rapid adsorption at the micropore pore mouth (i.e., no surface barrier), and activated diffusion in the micropore. This type of model was used by Sargent and Whitford (1971); Kawazoe et al. (1974); Shah and Ruthven (1977); Andrieu and Smith (1980); and Do (1983).

Later, Bulow et al. (1980); Koresh and Soffer (1981); and Fu et al. (1986) have all attempted to describe uptake in zeolite using a surface barrier model.

The objective of this work is to investigate the interplay between three rate processes: macropore diffusion, micropore diffusion and surface processes, in systems with a linear adsorption isotherm. In particular, the effects of particle size, microsphere size, and temperature are investigated.

Problem Formulation

Consider a particle adsorbent having a bimodal pore size distribution. The following assumptions are made in this theoretical analysis

- The particle and microsphere are spherical
- The diffusivities are constant
- The rate constants for adsorption and desorption are constant
- The system is isothermal

Having made these assumptions, the mass balances in nondimensional form for the adsorbate in the macropore and micropore are shown as model 1 in Figure 1. Parameters are defined in the nomenclature.

The parameters γ and B are dynamic parameters. The parameter γ is the ratio of the time scale for adsorption if macropore controls the uptake, to the time scale for adsorption if micropore controls the uptake in the absence of surface mass action. The relative magnitude of this surface mass action to the micropore diffusion is described by the parameter, B.

Since we have three rate processes described by two nondimensional parameters, γ and B, the controlling mechanism of the global uptake is dictated by the magnitude of these parameters. Depending on the magnitudes of these two parameters and their relative magnitude, there are six independent degenerate models from the parent model, Model 1. The governing equations of these models, and their parametric domain of validity are shown in Figure 1.

The parent model as well as the degenerate models are linear, and are solved by Laplace transform. Solutions for the fractional uptake and the half-time are tabulated in Table 1.

Discussion

Effect of parameter

Two parameters that dictate the controlling mechanism are the parameters B and γ. For a given system, if the particle size, R, increases, the parameter B will stay constant and the parameter γ will increase proportionally to the square of the particle radius. Therefore, the particle size effect can be easily seen in Figure 1.

To investigate temperature's effect on the switching of the controlling mechanism, we look at the temperature dependence

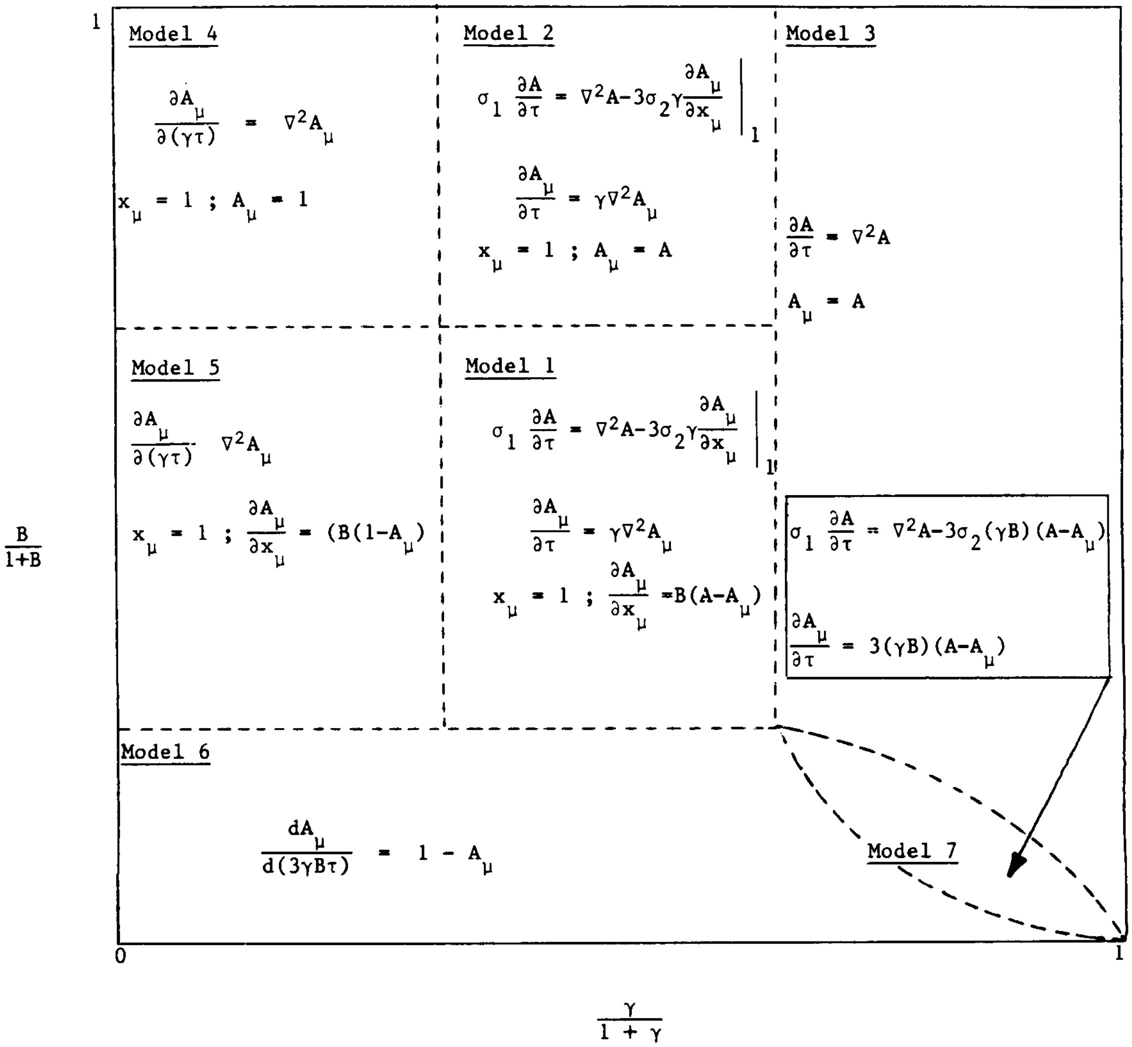

Figure 1. Parametric map of hierarchy of models in nondimensional form.

Model 1: Macropore-micropore diffusion-surface barrier
Model 2: Macropore-micropore diffusion
Model 3: Macropore diffusion
Model 4: Micropore diffusion
Model 5: Micropore diffusion-surface barrier
Model 6: Surface barrier
Model 7: Macropore diffusion-surface barrier

of the two parameters, B and γ. Parameter B depends on two rate parameters, k_d, and $\mathcal{D}$, which take the following functional form

$$k_d = k_{do}e^{-E_d/RT}, \quad \mathcal{D} = \mathcal{D}_o e^{-E_\mu/RT} \tag{1}$$

We shall assume that the activation of energy for adsorption is zero. Therefore, the heat of adsorption is equal to the activation energy for desorption. To study the effect of temperature, we consider three cases

$1: Q = E_d > E_\mu$
$2: Q = E_d < E_\mu$
$3: Q = E_d = E_\mu$

First, we look at case 1: $Q = E_d > E_\mu$. In this case

$$B = \frac{k_d R_\mu}{\mathcal{D}} = \frac{k_{do} R_\mu}{\mathcal{D}_o} \cdot \exp\left[-(E_d - E_\mu)/RT\right], \tag{2}$$

$$\gamma \simeq \frac{(1-\epsilon_M)K_o\mathcal{D}_o R^2}{\epsilon_M \mathcal{D}_p R_\mu^2} \exp\left[(Q - E_\mu)/RT\right] \tag{3}$$

we have ignored the term ϵ_M relative to the term $(1 - \epsilon_M)K$ in Eq. 3, which is true for all practical absorbents. Thus, in this case 1, the parameter B increases with temperature while the parameter γ decreases with increasing temperature. However, the product

$$B\gamma = \frac{(1-\epsilon_M)k_a R^2}{\epsilon_M \mathcal{D}_p R_\mu} \tag{4}$$

Table 1. Fractional Uptake and Half-time of Parent Model and Six Degenerate Models

Model	Solution
1	$F = 1 - \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} a_{nm} \exp(-\gamma\eta_{nm}^2\tau)$ $\tau_{0.5}$ obtained by setting F to ½
2	Same as Model 1 After Setting $B \rightarrow \infty$
3	$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty} n^{-2} \exp(-n^2\pi^2\tau)$ $\tau_{0.5} = 0.03055$
4	$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty} n^{-2} \exp(-n^2\pi^2\gamma\tau)$ $\tau_{0.5} = 0.03055/\gamma$
5	$F = 1 - \sum_{n=1}^{\infty} C_n \exp(-\zeta_n^2\gamma\tau)$ $\tau_{0.5}$ obtained by setting F to ½
6	$F = 1 - \exp(-3\gamma B\tau)$ $\tau_{0.5} = (\ln 2)/3\gamma B$
7	$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty} n^{-2} \exp\left[-\frac{3(\gamma B)\xi_n^2\tau}{\xi^2 + 3(\gamma B)}\right]$ $\tau_{0.5}$ obtained by setting F to ½

$$a_{nm} = \frac{18}{\xi_n^2} \cdot \frac{(\sin \eta_{nm} - \eta_{nm}\cos \eta_{nm})^2}{\eta_{nm}^4\left(\frac{1}{2} - \frac{\sin(2\eta_{nm})}{4\eta_{nm}}\right)}, \quad \xi_n = n\pi$$

$$\eta_{nm} \operatorname{cotan}(\eta_{nm}) - 1 = -\left(\frac{1}{B} + \frac{3\gamma}{\xi_n^2}\right)^{-1}$$

$$C_n = \frac{3(\sin \zeta_n - \zeta_n \cos \zeta n)^2}{\zeta_n^4\left(\frac{1}{2} - \frac{\sin 2\zeta_n}{4\zeta_n}\right)}, \quad \zeta_n \operatorname{cotan} \zeta_n - 1 = B$$

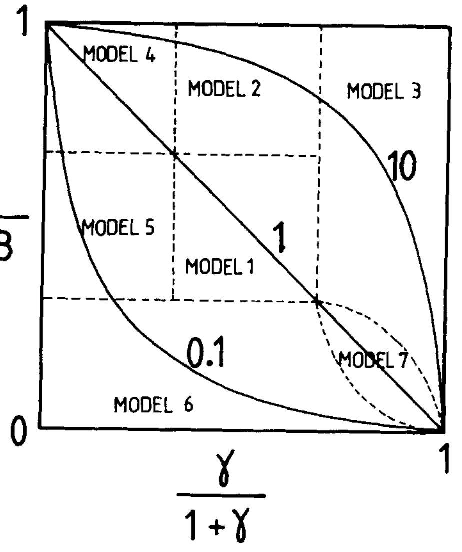

Figure 2. Plot of $B/(1 + B)$ vs. $\gamma/(1 + \gamma)$ with B as parameter.

is independent of temperature, if we ignore the temperature dependence of the macropore diffusivity. This seems reasonable because the temperature dependence of the macropore diffusivity is rather weak. Therefore, the product $B\gamma$ defined in Eq. 4 is independent of temperature. We show on Figure 2 a plot of $B/(1 + B)$ versus $\gamma/(1 + \gamma)$ with $B\gamma$ as a parameter. Thus, when

- $B\gamma$ is less than 0.1 (i.e., small particle size, small rate constant for adsorption, large microsphere, large diffusivity in macropore), the controlling mechanism switches from surface barrier control (model 6) to micropore diffusion-surface barrier (model 5) to micropore diffusion control (model 4), as temperature increases
- $B\gamma$ is greater than 10 (i.e., large particle size, high rate constant for adsorption, small microsphere, small diffusivity in macropore), the controlling mechanism switches from macropore diffusion control (model 3) to micropore-macropore diffusion control (model 2) to micropore diffusion control (model 4), as temperature increases
- $B\gamma$ is between 0.1 and 10, the controlling mechanism switches from macropore diffusion-surface barrier control (model 7) to macropore diffusion-micropore diffusion-surface barrier control (model 1) to micropore diffusion control (model 4), as temperature increases

Now, we look at case 2: $Q = E_d < E_\mu$. In this case, parameter B decreases with temperature while parameter γ increases with temperature. But the product $B\gamma$ is still independent of temperature. Thus, in this case the switching in the controlling mechanism is opposite to that in case 1. Finally, in case 3: $Q = E_d = E_\mu$,

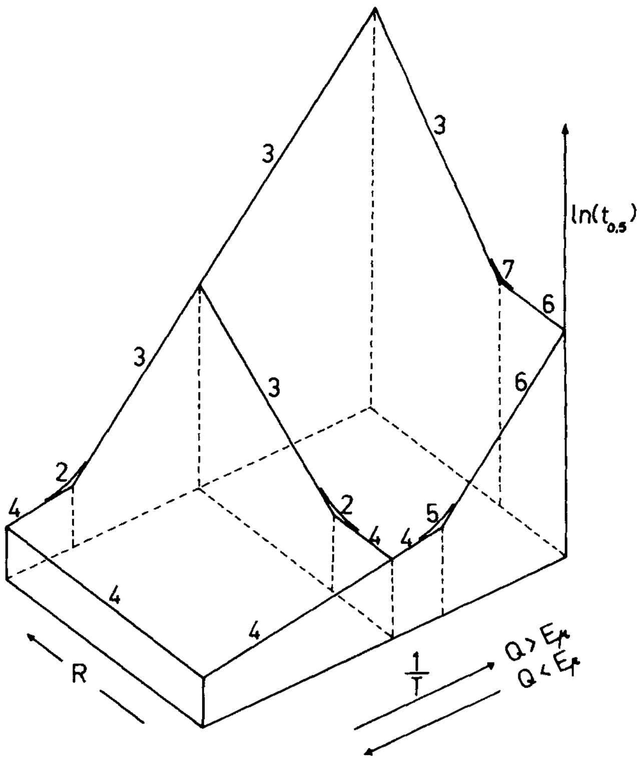

Figure 3. Plot of half-time, $t_{0.5}$, vs. particle radius R and $1/T$.

Table 2. Parameters for Adsorption of Benzene on HY Catalyst (Hattori and Murakami, 1974)

T (°C)	k_a (cm/s)	k_d (cm/s)	K	$\mathcal{D}_{100°C} = 1 \times 10^{-10}$		$\mathcal{D}_{100°C} = 1 \times 10^{-8}$		$\mathcal{D}_{100°C} = 1 \times 10^{-12}$ cm²/s	
				B	γ	B	γ	B	γ
100	4.53×10^{-3}	1.67×10^{-7}	27,126	0.167	1.07	0.00167	106.7	16.7	0.0107
150	4.53×10^{-3}	1.17×10^{-6}	3,872	0.327	0.45	0.00327	45.2	32.7	0.0045
200	4.53×10^{-3}	5.38×10^{-6}	842	0.550	0.23	0.00550	22.8	55.0	0.0023
250	4.53×10^{-3}	1.86×10^{-5}	244	0.841	0.13	0.00841	12.8	84.1	0.0013

the parameters B, γ, and $B\gamma$ are independent of temperature. Hence, the controlling mechanism does not vary with temperature.

The combined effect of the particle size and temperature on the half-time $t_{0.5}$ (the controlling mechanism) is best summarized in Figure 3 as a three dimensional plot of ln $t_{0.5}$ versus R and $1/T$. The number on the response surface denotes the model number. Thus, it can be seen in Figure 3 that model 4 (micropore diffusion control) and model 3 (macropore diffusion control) dominate most of the response surface. This is the reason why these two models are widely in the adsorption literature.

Investigation of system of benzene/HY zeolite

To illustrate our theory on the system of benzene/HY zeolite Hattori and Murkami, 1974, we have to assume values of the following parameters: $R_\mu = 1 \times 10^{-6}$ m, $\rho_\mu = 1{,}600$ kg/m³, $E_\mu = 33.4$ kJ/mol., $\epsilon_M = 0.4$, $\tau_M = 4$; and that the diffusion transport in macropore is by molecular motion. From Hattori and Murakami (1974), rate constants for adsorption and desorption are $k'_a = 85$ cm³/g/s, and $k'_d = 7 \times 10^4 \exp(-12{,}200/RT)$(s⁻¹). Converting these to our definition of rate constants, we obtain:

$$k_a = \frac{k'_a \rho_\mu R_\mu}{3} = 4.53 \times 10^{-5} \text{ m/s}$$

$$k_d = \frac{k'_d R_\mu}{3} = \frac{7}{3} \times 10^{-2} \exp\left(-\frac{12{,}200}{RT}\right) \text{m/s} \quad (8)$$

Since they did not report a value of diffusivity in micropore, we shall assume a value of 1×10^{-10} cm²/s at 100°C. Table 2 shows parameters for four different temperatures: 100, 150, 200 and 250°C, which cover the range carried out by Hattori and Murakami (1974). We note that the parameters B and γ are small. Hence, the proper model to describe their experiment is the surface barrier model, which is the one used in their analysis. For this assumed diffusivity the parametric domain of their experiment is shown in Figure 4 as Region A.

However, if we assume a value of 1×10^{-12} cm²/s at 100°C for micropore diffusivity, the parameter B is greater than 10 and γ is less than unity, Table 2. The controlling mechanism is micropore diffusion control (Region B of Figure 4). However, their experiment with inert gas, like propylene, has ruled out the possibility of micropore diffusion control. Thus, the diffusivity of benzene in Y zeolite at 100°C should be greater than 1×10^{-12} cm²/s.

Finally, for an assumed value of 1×10^{-8} cm²/s at 100°C for benzene in micropore, the calculated parameters B and γ are shown in Table 2. These values indicate that the controlling mechanism is the surface barrier process. The domain is shown in Figure 4 as shaded region C.

From this exercise, it seems fair to say that the diffusivity of benzene is of the order of or greater than 1×10^{-10} cm²/s at 100°C, which is comparable to a value of 2.4×10^{-10} reported by Doelle and Riekert (1981) for benzene in Pantasil zeolite at 30°C.

Investigation of other zeolite systems

First, we investigate the adsorption data of cyclo-C_3H_6 and 5A zeolite obtained by Haq and Ruthven (1986). Like most other workers, they ignored the surface barrier process in their model. We now would like to reevaluate their experimental results with the inclusion of this process. In the absence of the rate constant magnitude for adsorption for a cyclo-C_3H_6/5A system, we shall take two values of the rate constant of adsorption, 1×10^{-3} and 1×10^{-2} cm/s, as in the work of Hattori and Murakami (1974), who reported a value of 4.53×10^{-3} cm/s for their system of benzene/Y zeolite. Table 3 shows the calculated parameters B and γ for two values of adsorption rate constant. When the rate constant is 1×10^{-2} cm/s, the parameter γ is much less than unity, and the parameter B is much greater than unity. Therefore, their experimental data fall into the domain of model 4 (Region A in Figure 5), micropore diffusion control, which is what they assumed in their model. When the rate constant is 1×10^{-3} cm · s, the parameter γ is much less than unity and the parameter B is of the order of ten; this means that their experimental data fall between the domain of model 4 and model 5. Their system is still controlled by micropore diffusion but with some weak degree of adsorption-desorption barrier. This exercise establishes the necessity of obtaining the rate con-

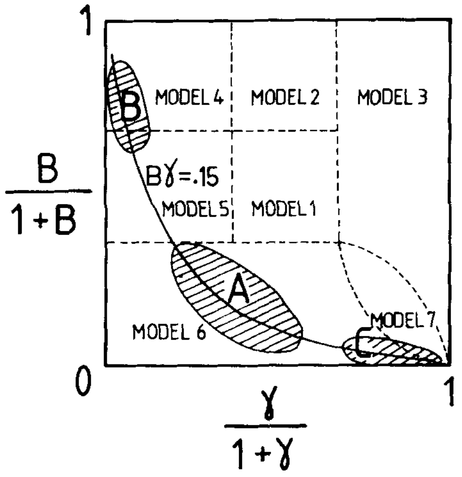

Figure 4. Parametric map of validity domain for adsorption of benzene on HY zeolite.

Table 3. Parameters for Adsorption of Cyclo C_3H_6 on 5A (Hag and Ruthven, 1986)
$\epsilon_M = 0.33$, $R_\mu = 1 \times 10^{-4}$ cm, $R = 0.025$ cm

T (°C)	K	$\mathcal{D}_p$ (cm² · s)	$\mathcal{D}$ (cm² · s)	$k_a = 1 \times 10^{-2}$ cm/s		$k_a = 1 \times 10^{-3}$ cm/s	
				B	γ	B	γ
300	33	0.452	3.1×10^{-10}	97.7	0.0029	9.77	0.0029
352	15	0.516	4.3×10^{-10}	155	0.0016	15	0.0016
380	10.4	0.544	4.7×10^{-10}	205	0.0012	20	0.0012

stant for adsorption in future work because its magnitude has an influence on the correct controlling mechanism of global adsorption uptake.

Next, look at the ethane/4A system of Carlson and Dranoff (1985). They used the micropore diffusion model at the outset to describe their experimental data. Since they did not report values for macropore porosity and crystal radius, we will assume a macropore porosity of 0.4 and a crystal radius of 1×10^{-4} cm. Table 4 shows the calculated parameters B and γ for two values of the rate constant for adsorption ($k_a = 1 \times 10^{-2}$ and 1×10^{-3} cm · s). For these two values the parameter γ is much less than unity and the parameter B is much greater than unity. Thus, their experimental ethane/4A data fall into the domain of model 4 (region C in Figure 5), a micropore diffusion control model, which is the one they used to describe their data. This conclusion is not surprising for 4A zeolite because of the extremely slow diffusion of adsorbate into the micropore of the zeolite crystal.

Finally, we evaluate the experimental data of C_3H_8/Na-Mordenite obtained at Ma and Mancel (1973). For two values of rate constant for adsorption ($k_a = 1 \times 10^{-2}$ and 1×10^{-3} cm/s), Table 5 shows the calculated parameters γ and B. The parameter B is much greater than unity and the parameter γ is of the order of unity, i.e., their experimental data fall into the domain of macropore-micropore diffusion control (model 2), which is the model they employed to analyze their experimental data. The simple exercise here confirms the correct choice of model in the analysis of their experimental data.

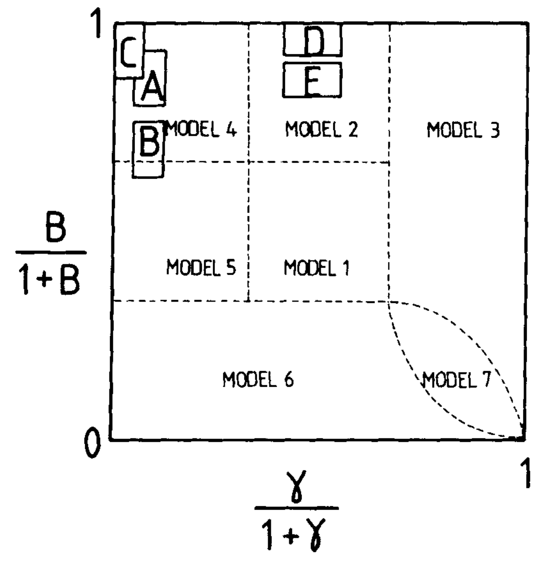

Figure 5. Parametric map of validity domain for various systems.

Cyclo–C_3H_6/5A
$R = 0.025$ cm
$R_\mu = 1 \times 10^{-4}$ cm
$A : k_a = 1 \times 10^{-2}$ cm/s
$B : k_a = 1 \times 10^{-3}$ cm/s

Ethane/4A
$R = 0.05$ cm
$R_\mu = 1 \times 10^{-4}$ cm
$C : k_a = 1 \times 10^{-4} - 1 \times 10^{-2}$ cm/s

C_3H_8/Na-Mordenite
$R = 0.0927$ cm
$R_\mu = 1 \times 10^{-4}$ cm
$D : k_a = 1 \times 10^{-2}$ cm/s
$E : k_a = 1 \times 10^{-3}$ cm/s

Table 4. Parameters for Adsorption of Ethane on 4A (Carlson and Dranoff, 1985)
$\epsilon_M = 0.4$, $R_\mu = 1 \times 10^{-4}$ cm, $R = 0.05$ cm

					$k_a = 1 \times 10^{-2}$ cm/s		$k_a = 1 \times 10^{-3}$ cm/s		$k_a = 1 \times 10^{-4}$ cm/s	
T (°C)	K	$\mathcal{D}_p$ (cm² · s)	$\mathcal{D}/R_\mu^2$ (s⁻¹)	γ	k_d (cm · s)	B	k_d (cm/s)	B	k_d (cm/s)	B
25	251	0.17	4×10^{-5}	0.00022	3.98×10^{-5}	9,960	3.98×10^{-6}	996	3.98×10^{-7}	99.6
50	135	0.193	8.3×10^{-5}	0.00022	7.41×10^{-5}	8,925	7.4×10^{-6}	893	7.4×10^{-7}	89.3
75	67	0.215	1.55×10^{-4}	0.000184	1.49×10^{-4}	9,629	1.5×10^{-5}	963	1.5×10^{-6}	96.3

Table 5. Parameters for Adsorption of C_3H_8 on Na-Mordenite (Ma and Mancel, 1973)
$\epsilon_M = 0.4$, $R_\mu = 1 \times 10^{-4}$ cm, $R = 0.0927$ cm

T (°C)	K	$\mathcal{D}_p$ (cm² · s)	$\mathcal{D}$ (cm² · s)	$k_a = 1 \times 10^{-2}$ cm/s		$k_a = 1 \times 10^{-3}$ cm/s	
				B	γ	B	γ
127	13	0.0008	5.4×10^{-11}	1,426	1.19	142.6	1.19
161	5.8	0.0011	9.7×10^{-11}	1,773	0.74	177.3	0.74
209	1.8	0.0015	1.64×10^{-10}	3,390	0.35	339	0.35

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Notation

A = adsorbate concentration in macropore, C/C_o
A_μ = adsorbate concentration in micropore, $C_\mu/C_{\mu o}$
B = parameter, $k_d R_\mu/\mathcal{D}$
C = adsorbate concentration in macropore, mol/cm^3
C_o = constant external adsorbate concentration, mol/cm^3
C_μ = adsorbate concentration in micropore, mol/cm^3
$C_{\mu o} = KC_o$
$\mathcal{D}$ = diffusivity in micropore, cm^2 · s
$\mathcal{D}_p$ = diffusivity in macropore based on void area, cm^2 · s
E_d = activation energy for desorption, (KJ/mol)
E_μ = activation energy for micropore diffusion, (KJ/mol)
k_a = rate constant for adsorption, cm · s
k_d = rate constant for desorption, cm · s
K = adsorption equilibrium constant, k_a/k_d
Q = heat of adsorption, KJ/mol
r = radial coordinate of the particle, cm
r_μ = radial coordinate of the microsphere, cm
R = particle radius, cm
R_μ = microsphere radius, cm
$x = r/R$
$x_\mu = r_\mu/R_\mu$

Greek letters

γ = parameter, $[\epsilon_M + (1 - \epsilon_M)K]\mathcal{D}R^2/(\epsilon_M \mathcal{D}_p)R_\mu^2$
ϵ_M = macropore porosity
ρ_μ = microsphere density
σ_1 = parameter, $\epsilon_M/[\epsilon_M + (1 - \epsilon_M)K]$
σ_2 = parameter, $1 - \sigma_1$
τ = time, $(\epsilon_M \mathcal{D}_p)t/R^2[\epsilon_M + (1 - \epsilon_M)K]$

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