Validity of Isothermality in Adsorption Kinetics of Gases in Bidispersed Solids

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Nonisothermal effects on the adsorption kinetics of ethane and propane in activated carbon are described for both single and binary systems. A heterogeneous macropore, surface and micropore diffusion model recently proposed by Hu and Do (1993) describes the mass-transfer rate processes of gases in a heterogeneous microporous bidispersed particle. The model is extended to cover nonisothermal effects by taking into account the energy balance around the particle system. Experimental uptake data of ethane and propane in Ajax activated carbon previously collected in our laboratory (Hu et al., 1993; Hu and Do, 1993) satisfy the isothermal criterion.

Theory

The physical system and assumptions in the model development are the same as those of Hu and Do (1993) with the additional heat balance equation. A lump thermal model, allowing for a uniform temperature within the particle, is assumed to describe the heat transfer between the particle and surroundings. The model equations are similar to those of Hu and Do (1993) with the following additional heat balance equation:

$$\rho_p C_{ps}\frac{dT_p}{dt}+ha_h(T_p-T_0)=(1-\epsilon_M)\sum_{j=1}^{NC}[-\Delta H(j)]\frac{d\overline{\overline{C}}_\mu(j)}{dt} \tag{1}$$

where ρ_p and C_{ps} are the apparent density and specific heat capacity of the particle, respectively, t is time, h is the particle-to-fluid heat-transfer coefficient, a_h is the heat-transfer area per unit volume of particle, T_p and T_0 are the temperatures inside the particle and in the bulk phase, ϵ_M is the macropore porosity of the particle, NC is the number of component (adsorbate), $-\Delta H$ is the heat of adsorption, which is the mean of the adsorption energy distribution, and $\overline{\overline{C}}_\mu$ is the amount adsorbed per unit volume of the particle.

The temperature dependency of the adsorbed species diffusivities has been determined via their relationship with the adsorption energy distribution in Hu and Do (1993). The variation of the pore diffusivity (D_p) is assumed to follow the following equation:

$$D_p=D_{p0}\left(\frac{T_p}{T_0}\right)^\beta \tag{2}$$

where D_{p0} is the pore diffusivity at the bulk temperature T_0. The value of β is 1.63 for ethane and 1.75 for propane in Ajax activated carbon.

The model equations are cast into nondimensional form using the nondimensional variables and parameters defined in Table 1 of Hu and Do (1993) and following additional variables and parameters for the purpose of numerical simulations:

$$\theta_p=\frac{T_p-T_0}{T_0};\quad \psi(k)=\frac{(1-\epsilon_M)C_{\mu 0}(k)[-\Delta H(k)]}{\rho_p C_{ps}T_0} \tag{3}$$

$$LeBi_h=\frac{hR^2a_h\left[\epsilon_M\sum_{j=1}^{NC}C_0(j)+(1-\epsilon_M)\sum_{j=1}^{NC}C_{\mu 0}(j)\right]}{C_{ps}\rho_p\left[\epsilon_M\sum_{j=1}^{NC}D_{p0}(j)C_0(j)+(1-\epsilon_M)\sum_{j=1}^{NC}D_{\mu 0}(j)e^{-a(j)\bar{\varepsilon}(j)}C_{\mu 0}(j)\right]} \tag{4}$$

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The heat balance equation in nondimensional form is:

$$\frac{d\theta_p}{d\tau} + LeBi_h\theta_p = \sum_{j=1}^{NC} \psi(j)\frac{d\overline{\overline{Y}}_\mu(j)}{d\tau} \tag{5}$$

The resulting nondimensional mass and heat balance equations are numerically solved by using a combination of an orthogonal collocation technique of Villadsen and Michelsen (1978) and a differential-algebraic equation solver (Petzold, 1982).

Experiments

The single and binary experimental data of ethane and propane in Ajax activated carbon collected in our laboratory (Hu et al., 1993; Hu and Do, 1993) are used in this article to test the validity of the isothermal assumption. The activated carbon particle used in our laboratory is a cylindrical extrudate with flat surfaces at each end. In the kinetic measurements selected surfaces were covered with epoxy so that the curvature effect on mass transfer could be studied. For example, if the cylindrical surface is covered with epoxy resin, the particle is of slab geometry in terms of mass transfer. However, in terms of heat transfer all surfaces (cylindrical and flat) are available. Therefore, the surface area per unit volume of particle for heat transfer is:

$$a_h = \left(\frac{1}{L} + \frac{2}{R}\right) \tag{6}$$

where L denotes the half-length of the slab sides and R is the radius of the cylinder.

Results and Discussion

The particle-to-fluid heat-transfer coefficient h is estimated via a correlation given by Wakao and Kaguei (1982):

$$Nu = 2.0 + 1.1Re^{0.6}Pr^{1/3} \quad (3 < Re < 1{,}000) \tag{7}$$

where Nu, Pr and Re are the Nusselt, Prandtl and Reynolds numbers and defined as follows:

$$Nu = \frac{h(2R)}{k_f}; \quad Pr = \frac{C_{pg}\mu}{k_f}; \quad Re = \frac{(2R)u\rho_g}{\mu} \tag{8}$$

where R is the radius of the particle, C_{pg}, μ and ρ_g are the specific heat capacity, kinematic viscosity and density of the gas, respectively, u is the gas superficial flow rate and k_f is the fluid thermal conductivity.

The nonisothermal effect on the adsorption kinetics of ethane and propane in Ajax activated carbon was first studied for single-component systems. The fastest adsorption rate observed in Hu et al. (1993) was the adsorption of 20% ethane in a 1/16-in. (1.6-mm)-dia. cylinder of Ajax activated carbon at 30°C, as shown in Figure 1a, where experimental data are shown as symbols. The equilibrium and dynamic parameters obtained by Hu et al. (1993) are used to produce simulation curves under both isothermal and nonisothermal conditions. The isothermal model simulations (Hu et al., 1993) are presented as solid lines, while the nonisothermal model simulations using the theory proposed in this article are plotted as dashed lines for both fractional uptake and particle temperature. Experimental data obtained at the adsorbate mixture flow rate of 500 cm^3/min were used here to calculate parameters necessary for the simulation of the nonisothermal model. The particle temperature change is about 2.5°C and its effect on the fractional uptake is negligible as one would expect for this use of high flow rate through the adsorption cell. Results of further tests at an adsorbate flow rate of 100 cm^3/min, which would be expected to exacerbate nonisothermality, are shown in Figure 1 as dashed-dotted lines. In this case a temperature increase of 4°C in adsorption (Figure 1a) or a decrease of 2°C in desorption (Figure 1b) is observed during the initial sorption process, which could be considered significant. Even with this significant change in temperature, the mass transfer is only affected marginally. This could be explained as follows. Although the pore diffusivity increases with temperature, this increase is partly compensated by the decrease in the adsorbed phase concentration, leading to the net effect of invariant fractional uptake with temperature (Figure 1 in Hu et al., 1993). Moreover, the decrease in the adsorbed concentration reduces the value of the surface diffusivity through its concentration dependency. This reduction is compensated by an increase of the surface diffusivity through the temperature dependent term, leading the same argument of invariant fractional uptake with temperature.

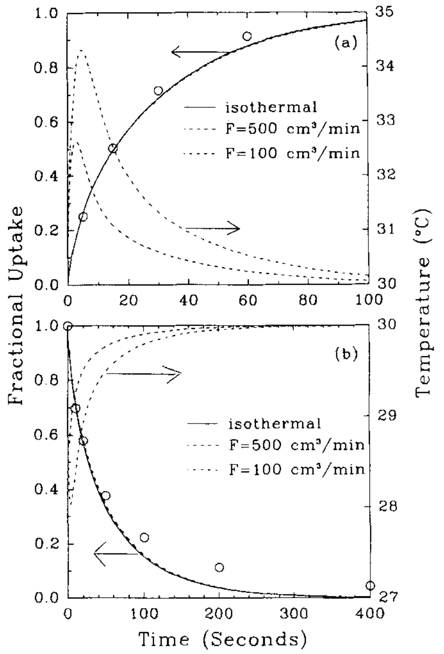

Figure 1. Sorption kinetics and particle temperature history of ethane in a 1/16 in. diameter cylinder of Ajax activated carbon at 30°C.

(a) 20% ethane adsorption; (b) 10% ethane desorption.

The 20% propane adsorption and 10% propane desorption kinetics in Ajax activated carbon of 1/16 in. diameter cylinder at 30°C are shown in Figure 2. Similar conclusions to

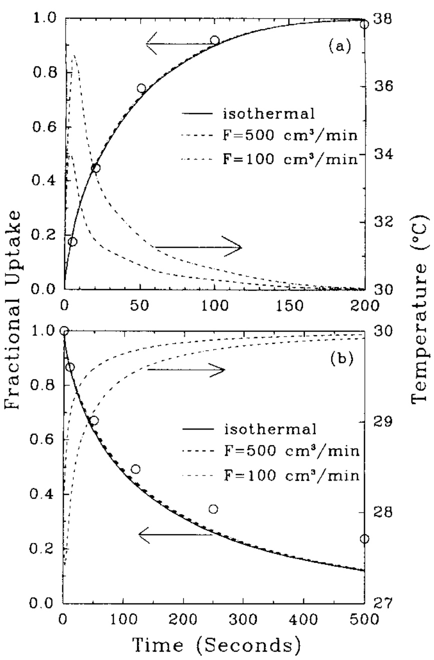

Figure 2. Sorption kinetics and particle temperature history of propane in a 1/16 in. diameter cylinder of Ajax activated carbon at 30°C.

(a) 20% propane adsorption; (b) 10% propane desorption.

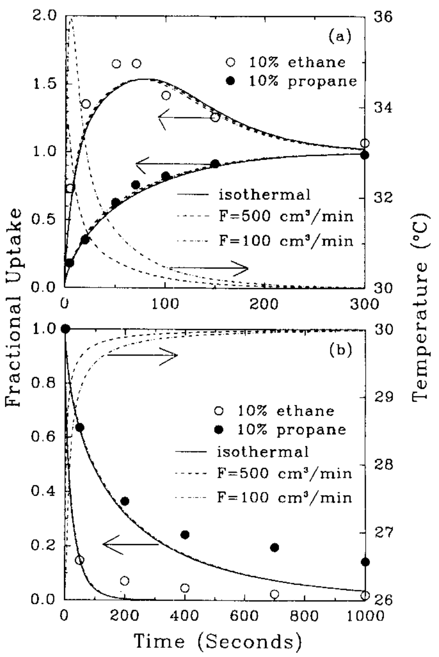

Figure 3. Binary sorption kinetics and particle temperature history of 10% ethane and 10% propane in a 1/16 in. diameter cylinder of Ajax activated carbon at 30°C.

(a) adsorption; (b) desorption.

those of ethane can be made here. The fractional uptake simulation of the nonisothermal model using a flow rate of 500 cm^3/min is superimposed to that of the isothermal model. Since the heat of adsorption in Ajax activated carbon is higher for propane than for ethane, the temperature change in the particle is more significant in the case of propane sorption than for ethane. The temperature rise can be as high as 7°C in the initial adsorption stage if a flow rate of 100 cm^3/min is used. Even in this case the sorption rate is only slightly affected.

We study next the nonisothermal effect on the binary sorption dynamics of ethane and propane in activated carbon. Figure 3 shows the adsorption and desorption kinetics of 10% ethane and 10% propane in Ajax activated carbon of 1/16 in. diameter cylinder. By using the equilibrium and dynamic parameters obtained for single-component, the model predictions are superimposed to each other for the isothermal and nonisothermal models. When an adsorbate flow rate of 100 cm^3/min is utilized, which corresponds to a 6°C temperature increase in adsorption or a 4°C decrease in desorption, the model predictions are only marginally improved. Since all the other sorption dynamics presented in Hu et al. (1993) and Hu and Do (1993) are slower than the cases studied here, it is reasonably safe to conclude that the isothermal assumption made in those two articles is justified.

Conclusions

A nonisothermal heterogeneous macropore, surface and micropore diffusion model is developed by taking into account the heat balance in the system. By using this model the isothermal assumption in the studies of Hu et al. (1993) and Hu and Do (1993) is at least theoretically justified. Although there are some temperature changes in the particle during the initial sorption stages, the effect of nonisothermal condition on the adsorption and desorption kinetics of ethane and propane in Ajax activated carbon is practically negligible.

Acknowledgment

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Notation

a = ratio of the surface activation energy to the heat of adsorption
a_h = surface area per unit volume of particle, m^2/m^3
C_{pg} = specific heat capacity of gas, J/(mol·K)
C_{ps} = specific heat capacity of the particle, J/(mol·K)
C_0 = characteristic concentration for the fluid concentration, kmol/m^3
$\overline{\overline{C_\mu}}$ = average adsorbed concentration in the particle, kmol/m^3
$C_{\mu 0}$ = characteristic concentration for the adsorbed concentration, kmol/m^3
D_p = macropore diffusivity, m^2/s
D_{p0} = macropore diffusivity at bulk temperature, m^2/s
D_μ = surface diffusivity, m^2/s
$D_{\mu 0}$ = surface diffusivity at zero energy level, m^2/s
$\bar{e}$ = mean nondimensional energy
F = flow rate of adsorbate mixture, m^3/s
h = particle to fluid heat-transfer coefficient, W/(m^2·K)
k_f = axial thermal conductivity, W/(m·K)
L = half-length of slab, m
$LeBi_h$ = nondimensional parameter defined in Eq. 4
R = particle radius, m
t = time, s

T_p = particle temperature, K
T_0 = bulk temperature, K
u = gas superficial flow rate, m/s
$\overline{Y_\mu}$ = average nondimensional adsorbed concentration in the particle

Greek letters

$-\Delta H$ = heat of adsorption, J/mol
θ_p = nondimensional temperature defined in Eq. 3
μ = kinematic viscosity
ρ_p = particle apparent density, kg/m^3
τ = nondimensional time
ψ = nondimensional parameter defined in Eq. 3

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