Anomalous Mass Transfer for Vapor Adsorption on Activated Carbon

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The phenomenon of surface transport has become widely recognized as a significant contributor to dynamic intraparticle mass transfer during adsorption. The object of this paper is to demonstrate and explain the occurrence of a dual breakthrough phenomenon for single-component adsorption, which had been observed by Cagliostro et al. (1985), in terms of a moving-boundary model for the rapid transport of an adsorbed vapor. The occurrence of this dual breakthrough phenomenon is shown to permit the separation of surface and volume diffusivities, which has not previously been possible (Riekert, 1985).

The surface flux of lighter gases has been characterized by surface hopping models and spreading pressure models (Okazaki et al., 1981), but the dynamics of adsorption of condensable vapors have been little characterized to date. Flood et al. (1952) found that surface transport of strongly adsorbed organic vapors was highest for the lowest partial pressures of the adsorbate, corresponding to the steepest region of their adsorption isotherm, and attributed this to a greater thermodynamic driving force for surface spreading. Flood termed the adsorbed vapor surface transport "anomalous." In more recent work, Thackur and Brown (1983) have indicated that a transition between the two types of surface fluid transport occurs with an increase in momentum transfer from the gas to the adsorbed fluid, and between fluid layers. The initial adsorption of mobile chemisorbed films has been suggested (Illinger and Rivin, 1970), so the assumption of physisorption is not necessary.

This paper considers two models for adsorption. The first, the moving-boundary model (MBM), considers transport of an organic vapor on activated carbon using an expression for the rate of surface spreading derived by Gilliland and Russell (1958),

$$n_s = \frac{-1{,}000 R T \rho_p A_p x^2}{C_R S_s k^2 P} \frac{dP}{dl_p} \tag{1}$$

where n_s is the adsorbed layer flow rate (kmol/s), P is the vapor pressure of the spreading film (kPa), l_p is a spatial coordinate (m) along the solid surface that incorporates the tortuosity factor k (dimensionless), A_p is the cross-sectional area of the porous material (m^2), S_s is the specific surface over which adsorbed molecules are mobile (m^2/kg), x is the surface concentration of the film at l_p (kmol/kg adsorbent), ρ_p is the apparent density of the solid (kg/m^3), R is the appropriate ideal gas constant, T is the absolute temperature (K), and C_R is Gilliland's coefficient of flow resistance. In dimensionless terms, this equation takes the form:

$$\eta_s = \frac{\alpha_g \sigma_p^2}{\gamma_p^*} \frac{\partial \gamma_p^*}{\partial \xi_p} \tag{2}$$

where σ_p is the surface concentration and η_s is the dimensionless spreading flux, α_g is a constant, and γ_p^* is the equilibrium concentration in a pore for a given surface concentration σ_p, as determined by the isotherm, and ξ_p is the spatial coordinate for the normal direction of spreading. The definitions of these and other dimensionless terms are given in Table 1.

The second model, the pore-volume diffusion model (PVDM) is more conventional with a pore diffusion transport term for gas adsorption in macroporous-microporous systems (Van Dongen and Stamperius, 1974; Do, 1983) and is used for qualitative comparison to the MBM and to show how this phenomenon may explain the dual breakthrough observations of Cagliostro et al. (1985). A mechanistic model similar to the PVDM was used by

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Table 1. Definition of Dimensionless Variables

$\alpha_g = \dfrac{-3{,}000\ RTW_eL}{\mathrm{MW}C_RS_sk^2R_p^2v}$	Dimensionless surface spreading mass transfer coefficient for Gilliland's expression
$\alpha_f = \dfrac{k_gLC_o}{W_ev}$	Dimensionless gas film mass transfer coefficient, where k_g is the dimensional film mass transfer coefficient
$\alpha_m = \dfrac{D_mL}{W_evR_m^2}$	Dimensionless diffusivity, where D_m is the micropore diffusivity, R_m is the mean micropore length, and W_e is the saturation capacity of the carbon at concentration C_o
$\alpha_p = \dfrac{D_pL}{vR_p^2}$	Dimensionless diffusivity, where D_p is the macropore diffusivity (a function of pore filling) and R_p is the mean pore length
$\alpha_s = \dfrac{kC_RL}{v\rho_pR_p}$	Dimensionless diffusivity, where k is the constant for Gilliland's equation for spreading pressure and ρ_p is particle density (kg/m^3)
$\gamma = \dfrac{C}{C_o}$	Dimensionless concentration, where C is a gas phase concentration and C_o is the challenge concentration at the entrance of the bed
$\eta_s = \dfrac{MWL}{v}\left(\dfrac{4}{3}\pi R_p^3\rho_pW_e\right)^{-1} n_s$	Dimensionless surface flux
$\rho_a = \dfrac{\rho_pa_sR_sL}{v\epsilon_pC_o}$	Dimensionless pore adsorption rate
$\rho_s = \dfrac{a_sR_sL}{vW_e}$	Dimensionless surface adsorption rate
$\sigma = \dfrac{q}{W_e}$	Dimensionless surface concentration
$\tau = \dfrac{vt}{L}$	Dimensionless time, where t is the time, v is the superficial velocity through the bed, and L is the bed length
$\xi = \dfrac{r}{r_o}$	Dimensionless radial coordinate where r is the actual coordinate and r_o is the maximal extent of r

Cagliostro et al. to explain their results in terms of residence time in the bed. Numerous experimental observations were conducted in the investigation reported here and extend the observation of dual breakthrough to times significantly in excess of residence time in the bed. For example, under some conditions the onset of dual breakthrough was observed after time intervals of about 1 min. with bed residence times of about 0.01 min. These observations were collected for a BPL carbon with about 30% of the pore volume as macropores, and 70% as micropores.

Moving-Boundary Model

Dubinin (1976), using soft X-ray photographs of the adsorption of bromobenzene by cylindrical activated carbon pellets, graphically demonstrated the nature of micropore and macropore transport control for vapor adsorption. Macropore transport control occurred at lower partial pressures of the adsorbate and resulted in the occurrence of a moving-boundary, or shrinking-core, type of adsorption within the particle. For this reason, and to account for short-term transient effects, the customary mass balance equations have been formulated as moving-boundary equations to investigate the transport of vapors by the surface diffusive mode. The corresponding mass balance equations for pore-volume diffusion were solved for the purpose of comparison and to assist in parameter estimation and were formulated with Damkohler's (1935) boundary conditions. A method of lines approach has been used to solve the moving-boundary surface diffusion with pore-volume diffusion equations, while a numerical inversion was used for the Laplace transform solution of the more conventional equations for pore-volume diffusion, assuming a linear isotherm approximation in the latter case. The effect of external mass transfer film resistance and axial dispersion has been included in both models. Figure 1 shows the computational nodes for the surface diffusion with pore-volume diffusion equations. The method of lines readily allows for the consideration of a moving boundary with this scheme because the boundary conditions are included as simple constraints on the dependent variables.

The particle-side mass balance equations for surface transport are as follows:

In Micropore.

$$\frac{\partial\sigma_m}{\partial\tau} = \alpha_m\left(\frac{\partial^2\sigma_m}{\partial\xi_m^2} + \frac{2}{\xi_m}\frac{\partial\sigma_m}{\partial\xi_m}\right) \tag{3}$$

Boundary conditions

$$\sigma_m = \sigma_m^*(\gamma_p), \quad \tau \geq 0, \quad \xi_m = 1 \tag{4}$$

$$\sigma_m = \frac{\partial\sigma_m}{\partial\tau} = 0, \quad \tau = 0, \quad \xi_m < 1 \tag{5}$$

$$\frac{\partial\sigma_m}{\partial\xi_m} = 0, \quad \tau \geq 0, \quad \xi_m = 0 \tag{6}$$

In Macropore.

Pore-volume contribution

$$\frac{\partial\gamma_p}{\partial\tau} = \alpha_p\left(\frac{\partial^2\gamma_p}{\partial\xi_p^2} + \frac{2}{\xi_p}\frac{\partial\gamma_p}{\partial\xi_p}\right) - \rho_a \tag{7}$$

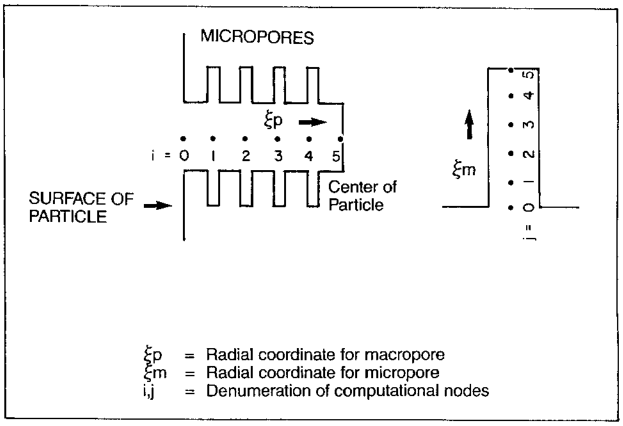

Figure 1. Computational nodes for moving-boundary formulation of surface transport with pore-volume diffusion.

Boundary conditions

$$\frac{\partial \gamma_p}{\partial \tau} = \alpha_f(\gamma_g - \gamma_p), \quad \tau \geq 0, \quad \xi_p = 1 \tag{8}$$

$$\frac{\partial \gamma_p}{\partial \tau} = \gamma_p = 0 \quad \tau = 0, \quad \xi_p < \xi_x \tag{9}$$

$$\frac{\partial \gamma_p}{\partial \xi_p} = 0 \quad \tau \geq 0, \quad \xi_p = 0 \tag{10}$$

Within the macropore, the effective diffusivity, α_p, is a function of pore filling.
Surface

$$\frac{\partial \sigma}{\partial \tau} = \frac{\partial \sigma_p}{\partial \tau} + \frac{\partial \sigma_m}{\partial \tau} = \alpha_s\left[\frac{\partial}{\partial \xi_p}\left(\frac{\sigma_p^2}{\gamma_p^*}\frac{\partial \gamma_p^*}{\partial \xi_p}\right) + \frac{2}{\xi_p}\frac{\sigma_p^2}{\gamma_p^*}\frac{\partial \gamma_p^*}{\partial \xi_p}\right] + \rho_s \tag{11}$$

Boundary conditions

$$\sigma_p = \sigma_p^*(\gamma_g), \tau \geq 0, \quad \xi_p = 1 \tag{12}$$

$$\sigma_p = \frac{\partial \sigma_p}{\partial \tau} = 0, \quad \tau = 0, \quad \xi_p < 1 \tag{13}$$

$$\frac{\partial \sigma_p}{\partial \xi_p} = 0, \quad \tau \geq 0, \quad \xi_p = 1 \tag{14}$$

$$\gamma_p^* = \gamma_p^*(\sigma) \text{ (isotherm equation)} \tag{15}$$

where γ_g is the bulk-phase concentration of the adsorbate, and γ_p^* is the equilibrium gas-phase concentration for the surface concentration σ_p in the macropores. The surface concentration in the micropores is σ_m. It is assumed that only one phase of the adsorbate exists within the micropores. The particle radial dimension is ξ_p, and the micropore radial coordinate is ξ_m. The dimensionless adsorption removal term for the macropores is ρ_a, while the corresponding dimensionless accumulation term for the macropore surface is ρ_s. The position of the moving boundary in the macropore, ξ_x, found by considering the relative rates of removal and accumulation, was fixed according to the method of Crank (1958) by a coordinate transformation, $\xi_p' = \xi_p/\xi_x$. The first stage of breakthrough was modeled by assuming initial adsorption as a monolayer, with subsequent pore filling.

Pore-Volume Diffusion Model

For the more conventional model considering only pore-volume diffusive transport and a linear isotherm for the particle, the mass balance equations were solved by Van Dongen and Stamperius (1974). The solution in the Laplace domain was given as the transfer function for the concentration challenging a packed bed as

$$\frac{C(s)}{C_o(s)} = \exp\left\{\frac{vX}{2D_g} - \frac{vL}{2D_g}\left[1 + \frac{4D_g}{v^2}\left(\frac{s + A_gK_g}{\epsilon_g}\right)\right]^{1/2}\right\} \tag{16}$$

where C is the exit concentration, C_o is the challenge concentration, D_g is the coefficient of axial dispersion, V is the superficial velocity in the bed, A_g is the specific area of an adsorbent particle, ϵ_g is the void fraction in the bed, K_g is a complex function including mass transfer parameters for the macro- and microporous regions, and s is a complex variable in the Laplace domain. $C_o(s) = 1$ for a pulse input, and $C_o(s) = 1/s$ for a step input, or fixed-challenge concentration. Equation 15 was inverted according to the method of Week (1966) and mass transfer parameters estimated by a least-squares fit to observed response breakthrough curve data for challenge at a fixed concentration to a packed bed. This parameter estimation technique for the PVDM provided initial estimates for parameter estimation utilizing the MBM.

Interparticle Transport

In both the MBM and PVDM, an axial dispersion model was incorporated. The crossflow model of Hinduja et al. (1980) was selected for the MBM because of its realistic depiction of the mechanism of axial dispersion as an exchange between stagnant and flowing regions of the fluid and the simplicity of the model equations which result from its application. A conventional Fickian model of axial dispersion was incorporated in the PVDM. The two approaches were compatible because parameters for Hinduja's model were estimated from those for the Fickian model, as described in the reference.

The external mass transfer film coefficient was estimated by the simple relationship of Petrovic and Thodos (1968) as a function of the Schmidt and Reynolds numbers.

Results and Conclusions

Figure 2 shows an experimental breakthrough curve observed for experimental tests with 1-bromobutane on Calgon BPL activated carbon, which exhibits the dual breakthrough phenomenon that has also been observed by Cagliostro (1985). It was necessary to utilize the more elaborate surface-transport coupled with pore-volume transport, called here the MBM, to fit the behavior of this curve. This is shown in Figure 3 for the initial breakthrough of Figure 2. The dual breakthrough phenomenon is then seen to be related to the short-term transient effects of the anomalous surface spreading of an adsorbed vapor. To reproduce these transient effects, the MBM formulation was necessary. To observe them it is necessary that data be taken at low breakthrough concentrations with a continuous analyzer, rather than a gas chromatography sampling analyzer, as noted by Cagliostro. The following conclusions may be drawn:

1. The effects of surface diffusive transport of adsorbed

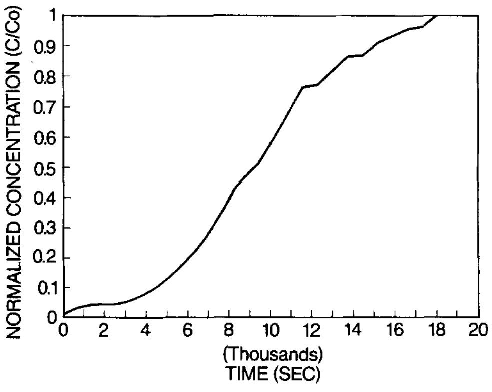

Figure 2. Dual breakthrough for a packed bed.

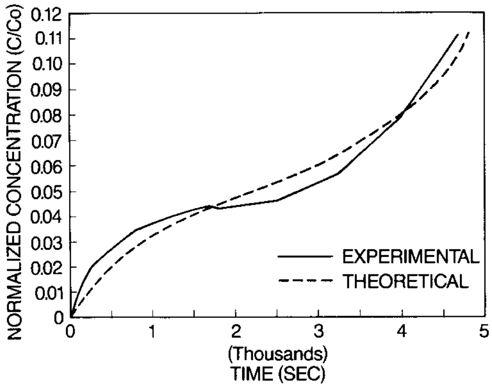

Figure 3. Dual breakthrough fit by a moving boundary model.

vapors are separable from pore-volume diffusion effects in packed adsorbent beds if transient data near the critical breakthrough concentration are taken.

2. The surface diffusive transport of higher molecular weight organic vapors is anomalous in that it may be related to a surface film spreading from a thermodynamic driving force related to isotherm shape rather than a simple activated diffusion with a well-defined diffusion coefficient.

3. The dual breakthrough phenomena observed by Cagliostro et al. (1985) can occur at times significantly in excess of the residence time in the bed and can be explained as a transient response to the anomalous surface spreading of an adsorbed vapor.

Notation

A = cross-sectional area for porous solid, m^2
a = specific surface area, m^2/kg
C = gas phase concentration, kg/m^3
C_R = coefficient of flow resistance, kg/s · m^2
d = particle size, m
D = axial dispersion coefficient, m^2/s, or diffusion coefficient, m^2/s
k = external film mass transfer coefficient, m^3/kg · s, or tortuosity factor
K = complex function involving mass transfer parameters in the Laplace domain
l = distance along surface of porous solid, m
L = bed length, m
n_s = adsorbed layer flow rate, kmol/s
MW = Molecular weight, kg/kmol
P = pressure, kPa
q = surface concentration of adsorbate, kg/kg adsorbent
r = radial coordinate for a spherical particle, m
R = ideal gas constant, kPa · m^3/kmol · K, or surface kinetic rate, kg/m^2 · s, used by Van Dongen (1974)
s = complex variable in Laplace domain
S = specific surface over which adsorbed molecules are mobile, m^2/kg
t = time, s
T = absolute temperature, K
v = superficial velocity, m/s
W = capacity of the adsorbent, kg adsorbate/kg adsorbent
W_e = saturation capacity of carbon, kg adsorbate/kg carbon, at gas-phase concentration C_o
x = local surface concentration of adsorbate, kmol/kg adsorbent
X = distance into bed, m

Greek letters

See Table 1

Subscripts

e = saturation at equilibrium
f = external film
g = gas phase in bed
m = micropore
p = macropore or particle
s = surface of macropore
x = moving boundary in macropore

Superscripts

$*$ = equilibrium value

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