EFFECTS OF CONCENTRATION DEPENDENCE OF SURFACE DIFFUSIVITY ON THE TRANSPORT AND ADSORPTION OF GASES IN A SOLID SPHERE WITH BIDISPERSE PORES

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Abstract – A model for transport and adsorption of gases in a biporous solid sphere was presented assuming a linear adsorption isotherm and linear concentration dependence of surface diffusivity. When put into dimensionless form this model is characterized by four dimensionless parameters. To help assessing the error involved in using constant effective diffusivities, numerical results were presented for the uptake of pure gases into a biporous solid sphere with concentration dependent diffusivity and compared with those for effective diffusivity model. The error in transient uptake was found to be as large as ten percent.

INTRODUCTION

Dynamics of adsorption for separation processes or for catalysis usually involves the flow of adsorbable gases into or out of porous adsorbents. Surface flow which is the migration of adsorbed molecules are known to be important in such flows.

When surface flow is modelled as a diffusive flow with concentration gradient as the driving force, surface diffusion coefficients may be determined. The surface diffusion coefficient is generally known to be a function which depends strongly on the surface concentration [1]. The concentration dependence is, however, in most cases ignored and a constant effective diffusion coefficient for both bulk and surface flow is employed. An analytic solution with a linear adsorption isotherm and a constant diffusion coefficient is available for a biporous solid sphere [2]. Analysis of concentration effect for uniform pore systems is provided recently by Kapoor and Yang [3]. The solution with a concentration dependent diffusion coefficients has to be obtained by numerical methods which may become very tedious.

The objective of this work is to develop a model for flow of pure gases in a biporous solid with a linear adsorption isotherm and concentration dependent diffusion coefficients, to present the results in a form suitable for assessing the effect of the concentration dependence and to discuss the concentration effect.

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THE MODEL

1. Structure

Consider a spherical pellet of apparent volume V_p and diameter R_p which consists of spherical particles with diameter R_c and total apparent volume V_c. ε_a is the void fraction of macropores in the pellet and ε_i is the void fraction of micropores inside a particle. Then V_p and V_c are related by the following relation.

$$V_c = V_p(1 - \varepsilon_a) \tag{1}$$

Also the total void fraction ε_t is given by

$$\varepsilon_t = \varepsilon_a + (1 - \varepsilon_a)\varepsilon_i \tag{2}$$

S_a and S_i are surface areas exposed to macropores and micropores per unit apparent volume of pellet and particles, respectively. We define fractions of surface areas exposed to macropore and micropore as follows.

$$f_a = S_a/S_t \tag{3}$$

$$f_i = S_i/S_t \tag{4}$$

where S_t is the total surface area per unit pellet volume which may be given by the relation $S_t = S_a + S_i(1 - \varepsilon_a)$. It follows that

$$1 = f_a + f_i(1 - \varepsilon_a) \tag{5}$$

2. Equilibrium Relation

We assume a linear adsorption isotherm which is given as follows.

$$q_t = KC \qquad (6)$$

Here q_t is the total amount adsorbed in the unit volume of pellet, C is the gas phase concentration based on pore volume and K is the equilibrium constant. Then q_i and q_a, which denote the amount adsorbed on the surfaces of micropore and macropore per unit apparent volume of pellet and particles, respectively, are given as

$$q_i = Kf_iC_i \qquad (7)$$

$$q_a = Kf_aC_a \qquad (8)$$

where C_i and C_a are gas phase concentration in micropores and macropores. Using Eq. (5) q_t may be written as

$$q_t = q_a + q_i(1 - \varepsilon_a) \qquad (9)$$

3. Mass Flux

Total flux J^t is the sum of gas phase flux J^g and surface flux J^s. The fluxes are assumed to be represented by the following forms in micropores and macropores.

$$J_h^g = -\varepsilon_h D_h^g(\partial C_h/\partial r_h) \qquad (h = a \text{ or } i) \qquad (10)$$

$$J_h^s = -D_h^s(\partial q_h/\partial r_h) = -\varepsilon_h D_h^s(Kf_h/\varepsilon_h)(\partial C_h/\partial r_h) \qquad (h = a \text{ or } i) \qquad (11)$$

Here D_h^g and D_h^s are diffusivities for bulk and surface flow. Then

$$J_h^t = -\varepsilon_h(D_h^g + D_h^s K_h)(\partial C_h/\partial r_h) \qquad (h = a \text{ or } i) \qquad (12)$$

where $K_h = Kf_h/\varepsilon_h$.

Now we assume surface diffusivities are the same in both type of pores and conveniently represented by a linear function of fractional amount adsorbed θ_h relative to a reference coverage.

$$D_h^s = D_0^s + D_1^s \theta_h \qquad (13)$$

Substituting Eq. (13) into (12) we have

$$J_h^t = -\varepsilon_h D_h[1 + \rho_h(\theta_h - 0.5)](\partial C_h/\partial r_h) \qquad (h = a \text{ or } i) \qquad (14)$$

where D_h is the effective diffusivity taken at $\theta_h = 0.5$.

$$D_h = (D_h^g + D_0^s K_h + 0.5 D_1^s K_h) \qquad (15)$$

$$\rho_h = D_{h1}^s K_h/D_h \qquad (16)$$

4. Mass Balance

Writing the total mass balances in the angle independent spherical coordinates we have for micropores

$$\partial N_i/\partial t = -(1/r_c^2)(\partial/\partial r_c)(r_c^2 J_i^t) \qquad (17)$$

and for macropores

$$\partial N_a/\partial t = -(1/r_p^2)(\partial/\partial r_p)(r_p^2 J_a^t) + [3(1-\varepsilon_a)/R_c]J_i^t(r_c = R_c) \qquad (18)$$

where r_c and r_p are distances from the center of particles and pellets, respectively and N_i and N_a are amounts of gases per unit volume in each type of pores defined as

$$N_h = \varepsilon_h C_h + q_h = \varepsilon_h(1 + K_h)C_h \qquad (h = a \text{ or } i) \qquad (19)$$

and the total amount per unit volume N_t is given by

$$N_t = N_a + (1 - \varepsilon_a)N_i \qquad (20)$$

Substituting Eqs. (14) and (19) into Eqs. (17) and (18) and putting these equations into dimensionless forms we have

$$(1/\delta)\partial\theta_i/\partial\varphi = (1/\eta_c^2)(\partial/\partial\eta_c)[(1 + \rho_i\{\theta_i - 0.5\})\eta_c^2(\partial/\partial\eta_c)\theta_i] \qquad (21)$$

$$\partial\theta_a/\partial\varphi = (1/\eta_p^2)(\partial/\partial\eta_p)[(1 + \rho_a\{\theta_a - 0.5\})\eta_p^2(\partial/\partial\eta_p)\theta_a] - \nu[(1 + \rho_i\{\theta_i - 0.5\})(\partial/\partial\eta_c)\theta_i]\eta_c = 1 \qquad (22)$$

where

$$\varphi = D_a t/(1 + K_a)R_p^2 \qquad (23)$$

$$\delta = [D_i/(1 + K_i)R_c^2]/[D_a/(1 + K_a)R_p^2] \qquad (24)$$

$$\nu = [3(1 - \varepsilon_a)\varepsilon_i/\varepsilon_a](D_i/R_c^2)/(D_a/R_p^2) \qquad (25)$$

$$\eta_c = r_c/R_c, \qquad \eta_p = r_p/R_p \qquad (26)$$

$$\theta_i = C_i/C_R, \qquad \theta_a = C_a/C_R \qquad (27)$$

C_R can be any fixed reference value and D_{ih}^s depends on the choice of C_R.

When ρ_i and ρ_a equal to zero, Eqs. (21) and (22) reduces to the forms given by Ruckenstein [2] although definitions of dimensionless variables are slightly different.

ESTIMATION OF PROPERTY VALUES

1. Structural Parameters

When needed property values are not available, we may use pore analysis data which usually provide us with average pore radii $\langle r_i \rangle$ and $\langle r_a \rangle$ and void fractions ε_i and ε_a. Also macroscopic values V_p and R_p for pellets can be directly determined. If we assume piecewise cylindrical pores, S_a and S_i can be found.

$$S_a = 2\varepsilon_a/\langle r_a \rangle, \qquad S_i = 2\varepsilon_i/\langle r_i \rangle \qquad (28)$$

With these values for S_a and S_i, f_i and f_a defined by Eqs. (3) and (4) are readily calculated using experimental ε_a.

R_c can be determined as follows. For the number

Table 1. Adsorption equilibrium constants and linear concentration dependent surface diffusivities for selected systems

Gas	Solid	Surface Area	Solid Density	T	D^s_{h0}	D^s_{h1}	K/S_{tr}	Maximum pressure	Data reference
		m^2/g	kg/m^3	K	m^2/s	m^2/s	m^3/m^2	mmHg	
C_2H_4	Vycor	117	1966	303	1.14×10^{-9}	7.86×10^{-9}	1.11×10^{-12}	566.88	[8]
C_3H_6	Vycor	117	1966	303	1.60×10^{-9}	3.80×10^{-9}	1.45×10^{-12}	262.66	[8]
iC_4H_{10}	Vycor	117	1966	303	1.95×10^{-9}	4.02×10^{-9}	1.34×10^{-12}	285.33	[8]
SO_2	Vycor	117	1966	303	–	–-	2.89×10^{-13}	71.99	[8]
Ar	Carbon	933	2120	273	4.07×10^{-8}	1.06×10^{-8}	3.16×10^{-14}	359.23	[9]
Ar	Carbon	933	2120	298	5.47×10^{-8}	5.80×10^{-9}	1.90×10^{-14}	359.98	[9]
Ar	Carbon	839	2120	273	1.3×10^{-8}	1.00×10^{-9}	3.94×10^{-14}	–	[9]
Ar	Carbon	839	2120	298	1.67×10^{-8}	1.30×10^{-9}	2.41×10^{-14}	–	[9]
N_2	Carbon	933	2120	273	4.29×10^{-8}	1.36×10^{-8}	3.57×10^{-14}	–	[9]
N_2	Carbon	933	2120	298	6.13×10^{-8}	3.27×10^{-8}	2.01×10^{-14}	–	[9]
N_2	Carbon	839	2120	273	1.53×10^{-8}	4.30×10^{-9}	5.20×10^{-14}	400.09	[9]
N_2	Carbon	839	2120	298	2.08×10^{-8}	3.20×10^{-9}	3.73×10^{-14}	499.92	[9]
Kr	Carbon	933	2120	273	8.01×10^{-9}	1.49×10^{-8}	1.65×10^{-14}	299.62	[9]
Kr	Carbon	933	2120	298	1.37×10^{-8}	1.38×10^{-8}	1.16×10^{-13}	429.30	[9]
Kr	Carbon	839	2120	273	5.25×10^{-9}	3.15×10^{-9}	–	–	[9]
Kr	Carbon	839	2120	298	7.58×10^{-9}	2.52×10^{-9}	1.19×10^{-13}	379.12	[9]
CO_2	Vycor	163	2083	223	–	–	1.87×10^{-11}	62.03	[10]
CO_2	Vycor	163	2083	195	–	–	5.05×10^{-13}	9.08	[10]
NH_3	Vycor	163	2083	298	–	–-	3.57×10^{-12}	16.00	[10]
NH_3	Vycor	163	2083	313	–-	–	3.74×10^{-12}	22.06	[10]

of particles per unit pellet volume N,

$$V_c/V_p = (4/3)\pi R_c^3 N, \qquad S_a = 4\pi R_c^2 N$$

from which we have

$$R_c = 3V_c/S_a = 3(V_p/S_a)(V_c/V_p) = (3/2)(1 - \varepsilon_a)\langle r_a \rangle / \varepsilon_a \quad (29)$$

2. Equilibrium Constant

K value defined in Eq. (3) is an experimental value. However in the absence of experimental data, we may estimate this value from that of similar gas-surface system at the same temperature. In this case appropriate conversion is needed.

$$K = (K_r/S_{tr})S_t \quad (30)$$

where (K_r/S_{tr}) is the K value of a reference system per unit surface area per unit pellet volume. Note that the amount adsorbed per unit surface area at constant pressure and temperature should be approximately same for a similar pair of gas-surface systems with different surface areas per unit pellet volume. Some values of (K_r/S_{tr}) are listed in Table 1.

3. Diffusivities

Following expression is proposed for bulk diffusion in pores [4].

$$D_h^g = (1/\tau_{gh})[D_{kh}(K_{nh} + W)/(K_{nh} + 1)]$$

$$+ \langle r_h \rangle R_g T C_h / 8\mu] \quad (31)$$

where the subscript h indicates either a for macropores or i for micropores and w is approximately a constant whose value is 0.9. If the Knudsen number $K_n (= \lambda/2\langle r_h \rangle)$ is much larger than one at low pressure, Eq. (31) becomes

$$D_h^g = (1/\tau_h^g)D_{kh} = [4\langle r_h \rangle / 3\tau_h^g][2R_g T/\pi M_w]^{0.5} \quad (32)$$

The tortuosity factor τ_h^g cannot be determined directly. It is usually in the range of 3 and 7 [5]. However, when we use Eq. (28) for estimation purpose, we may take $\tau_h^g = 5$ as a first guess.

If the pressure is not very low and/or $\langle r_h \rangle$ is large, the second term in Eq. (31) may become important. Then we may lump the concentration dependence of this term into the concentration dependence of surface diffusion term as,

$$D_h^s = D_0^s + (D_1^s + \langle r_h \rangle^2 R_g T/8 C_R \mu K_h \tau_h^g)\theta_h \quad (33)$$

Note that gas viscosity is almost pressure independent. One possible simplification is to assume that surface diffusivities are the same in both pores. Then Eq. (33) may be put into the form

$$D_h^s = (D_0^s + 0.5 D_{h1}^{sp}) + D_{h1}^{sp}(\theta_h - 0.5) \quad (34)$$

where

$$D_{h1}{}^{sp} = D_1{}^s + \langle r_h \rangle R_g T / 8 C_R \mu K_h \tau_h{}^g \qquad (35)$$

in which case Eqs. (15) and (16) are modified as

$$D_h = (D_h{}^g + D_0{}^s K_h + 0.5 D_{h1}{}^{sp} K_h) \qquad (36)$$

$$\rho_h = D_{h1}{}^{sp} K_h / D_h \qquad (37)$$

Although theories are available for the prediction of surface diffusion coefficients [6, 7], the applicability is limited. Two types of the concentration dependence are usually observed; one is monotonic increase and the other is gradual decrease followed by a sudden increase near monolayer coverage. The former may be approximated as a linear function of surface coverage θ_h. The linearly approximated values of $D_0{}^s$ and $D_1{}^s$ for some systems are also listed in Table 1. If the equilibrium pressure(P_e) is different from the maximum pressure(P_m) indicated in the table, $D_{1r}{}^s$ should be corrected as follows.

$$D_1{}^s = D_{1r}{}^s (P_e / P_m) \qquad (38)$$

MODEL CALCULATION

Eqs. (21) and (22) can be solved simultaneously for suitable initial and boundary conditions, namely,

$$\theta_i(0, \eta_c, \eta_p) = 0 \qquad \theta_a(0, \eta_p) = 0$$
$$\theta_i(0, 1, \eta_p) = \theta_a(0, \eta_p) \qquad \theta_a(0, 1) = 1$$
$$\partial\theta / \partial\eta_c = 0 \text{ for } \eta_c = 1 \qquad \partial\theta / \partial\eta_p = 0 \text{ for } \eta_p = 1 \qquad (39)$$

and an average uptake $\langle \theta_t \rangle$ at the dimensionless time φ can be computed.

$$\langle \theta_t \rangle = 3 \int [(1 + K_a)\varepsilon_a\theta_a + (1 + K_i)\varepsilon_i\langle\theta_i\rangle(1 - \varepsilon_a)]\eta_p{}^2 d\eta_p$$
$$/[(1 + K_a)\varepsilon_a + (1 + K_i)\varepsilon_i(1 - \varepsilon_a)]$$
$$= 3 \int [\theta_a + (v/3\delta)\langle\theta_i\rangle]\eta_p{}^2 d\eta_p / [1 + v/3\delta] \qquad (40)$$

where $\langle \theta_i \rangle = 3 \int \theta_i \eta_c{}^2 d\eta_c$

Explicit finite difference scheme based on three level Dufort-Frankel method [8] was used for numerical computation. $\Delta\eta = 0.1$ for both pores and $\Delta\varphi$ ranging from 10^{-2} to 10^{-5} depending on the value of v gave results which agree very closely with Ruckenstein's analytical series solution [2] with concentration independent diffusion coefficients.

The solution can be represented using four parameters(δ, v/δ, ρ_a and ρ_i). δ is the ratio of micropore conductance to that of macropore. v/δ value is proportional to the ratio of the number of molecules in micropores to that in macropores in equilibrium.
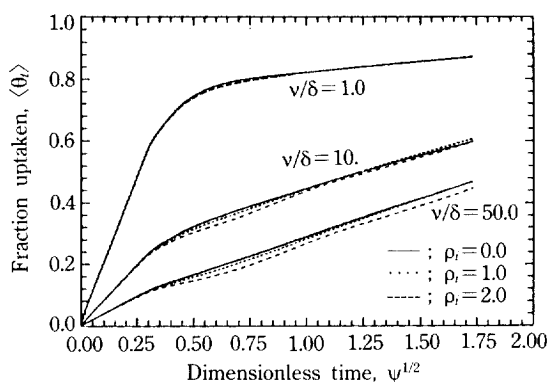

Fig. 1. Fractional uptake as a function of dimensionless time for $\delta = 1.0 \times 10^{-2}$ and $\rho_a/\rho_i = 0.0$.
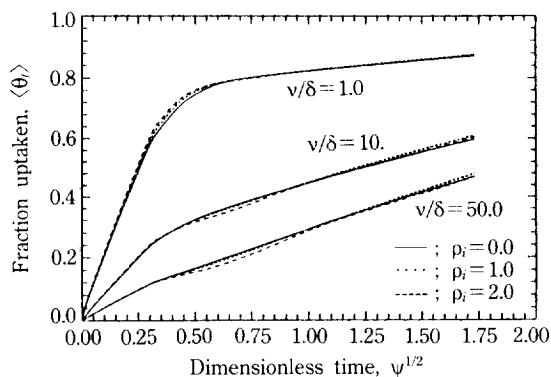

Fig. 2. Fractional uptake as a function of dimensionless time for $\delta = 1.0 \times 10^{-2}$ and $\rho_a/\rho_i = 0.5$.

$$v/\delta = [3(1 - \varepsilon_a)\varepsilon_i/\varepsilon_a][(1 + K_i)/(1 + K_a)] \qquad (41)$$

Then ρ_i or ρ_a which is defined by Eq. (16) or (37) is the ratio of concentration dependent term to the effective diffusivity and can vary from zero to two independent of effective diffusivity D_i or D_a. When diffusivities are concentration dependent, $(D_0{}^s + 0.5 D_{h1}{}^{sp})$ remains constant but $D_0{}^s$ and $D_{h1}{}^{sp}$ vary.

RESULTS AND DISCUSSION

Figs. 1 to 9 show the calculated results $\langle \theta_t \rangle$ as a function of dimensionless time φ for given set of parameters δ, v/δ, ρ_a/ρ_i and ρ_i. The curves for $\rho_i = \rho_a = 0$ corresponds to the reference solution with the constant effective diffusivity and denoted as $\rho_i = 0$ in figures. These figures may be used for estimating the effect of concentration dependence of surface diffusivity. The maximum error involved is approximately ten percent.

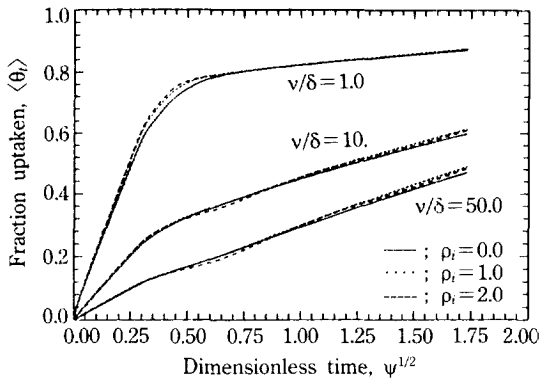δ value indicates the controlling transport mech-

Fig. 3. Fractional uptake as a function of dimensionless time for $\delta = 1.0 \times 10^{-2}$ and $\rho_a/\rho_i = 1.0$.
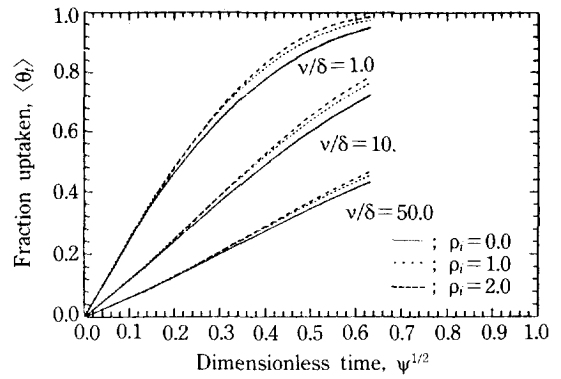

Fig. 6. Fractional uptake as a function of dimensionless time for $\delta = 1.0$ and $\rho_a/\rho_i = 1.0$.
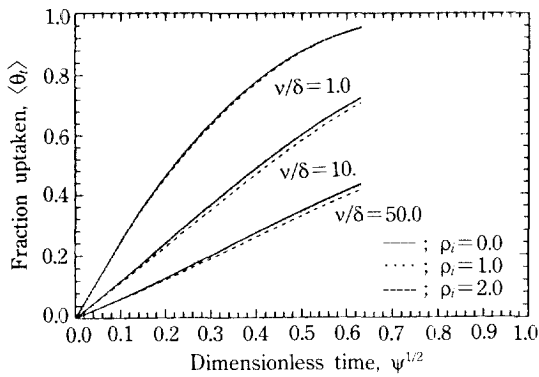

Fig. 4. Fractional uptake as a function of dimensionless time for $\delta = 1.0$ and $\rho_a/\rho_i = 0.0$.
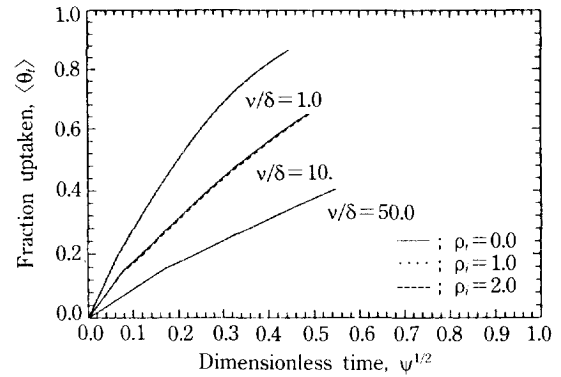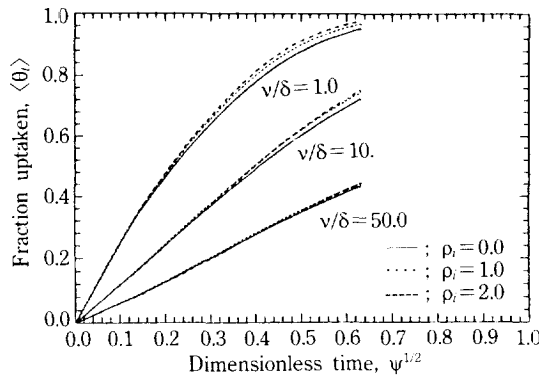

Fig. 7. Fractional uptake as a function of dimensionless time for $\delta = 1.0 \times 10^2$ and $\rho_a/\rho_i = 0.0$.

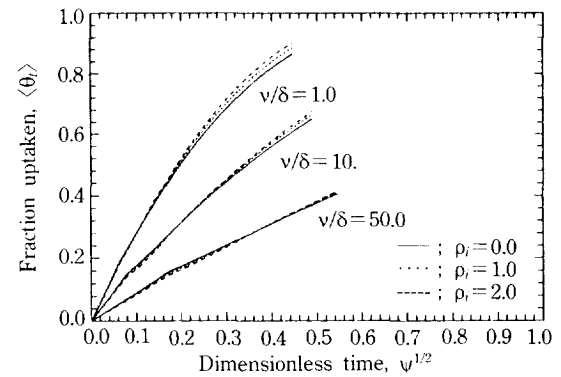Fig. 5. Fractional uptake as a function of dimensionless time for $\delta = 1.0$ and $\rho_a/\rho_i = 0.5$.

Fig. 8. Fractional uptake as a function of dimensionless time for $\delta = 1.0 \times 10^2$ and $\rho_a/\rho_i = 0.5$.

anism [2]. In systems with large δ value, macropore diffusion is controlling and all surface area is effectively exposed to macropore. In systems with small δ value, micropore diffusion is controlling and diffusion takes place in two steps; in the first step macropore is filled and in the second step slow micropore diffusion is dominating. Approximate analytical solutions are available for each extreme cases [4]. Intermediate
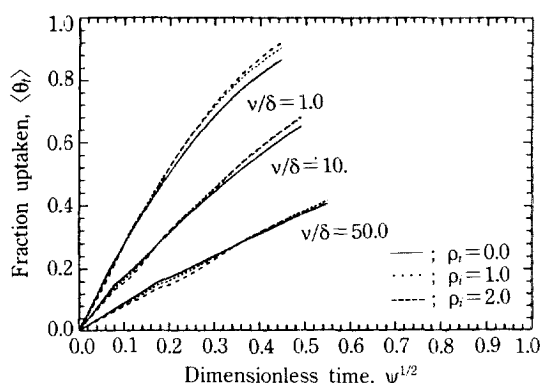
Fig. 9. Fractional uptake as a function of dimensionless time for $\delta = 1.0 \times 10^2$ and $\rho_a/\rho_i = 1.0$.
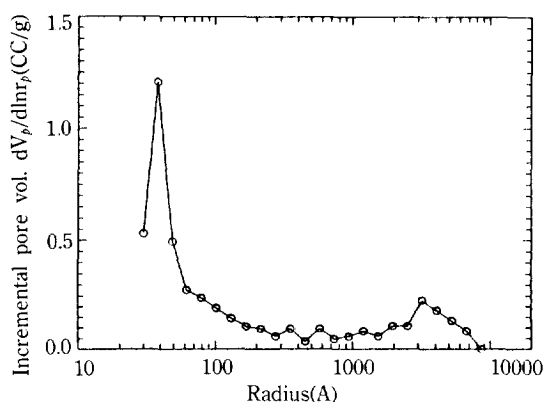

Fig. 11. Comparison of predicted and fitted uptake curves for a silica-gel pellet.

Fig. 10. Pore volume distribution function as a function of ln r.

values of δ(say $0.01 < \delta < 100$) indicate that both pore need to be considered for transport.

Silica gel is known to have a biporous structure when pelletized [9]. In an experiment described elsewhere [10], a silica gel sphere with 0.0042m radius was prepared by pelletizing ground silica gel. Pore analysis by mercury porosimetry indicated that $\varepsilon_t = 0.696$, $\varepsilon_a = 0.199$, $\langle r_t \rangle = 5.5 \times 10^{-9}$m and $\langle r_a \rangle = 2.152 \times 10^{-7}$m. Equilibrium pressure was 62.9 mmHg. Pore size distribution obtained using Micromeritics model 9305 is shown in Fig. 10 based on the contact angle of 135°. This distribution function when multiplied by d(lnr) gives the pore volume between the pore radius r and $r + dr$. Total surface area by porosimetry is 312.5 m²/g which may be compared with 278.1 m²/g by BET method. True density of silica gel was measured to give 1.920 g/cm³.

Value of K for ethylene and vycor system at 303 K is obtained from the values given Table 1 using the

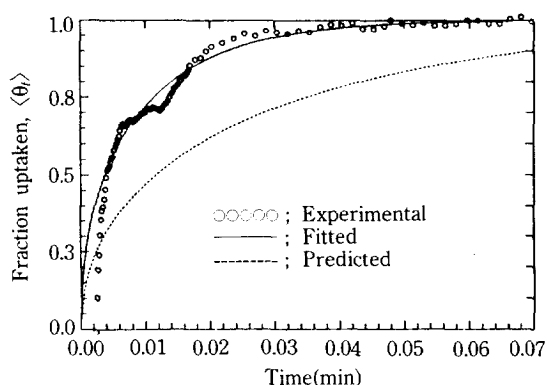calculated S_t. D_0^s and D_1^s for the same system can also be obtained from the table. Surface diffusion coefficient data are not available for ethylene-silica gel system. Surface of silica gel and that of vycor are known to be basically similar [9]. The experimental equilibrium constant for ethylene-silica gel system is found consistent with that for ethylene-vycor system. Applying the method described in the previous section and assuming the tortuosity factor τ_h^g equals five, we obtained the following values; $\delta = 3.55 \times 10^4$, $v/\delta = 63.57$, $\rho_a/\rho_i = 0.03$, $\rho_i = 2.5 \times 10^{-3}$ and $\phi/t = 2.94$.

Very small values of ρ_a/ρ_i and ρ_i indicate that constant effective diffusivities are justified. Large δ value indicate that the macropore diffusion is controlling. Therefore this biporous system may be assumed as a uniform macropore system with constant effective diffusion coefficient. We can go further. Since the δ value is very large and ρ values very small, an approximate analytical solution [2] may be used. The result is shown in Fig. 11 as the predicted curve. Agreement improves if we take $\tau_h^g = 1.3$ instead of 5.0 as shown in the figure as the fitted curve. Although such an agreement with experimental data is not generally expected, the proposed method is helpful in determining the effect of concentration dependence and the mechanism of pore transport.

CONCLUSION

For the adsorption of gases into biporous solid spheres with linear adsorption isotherm and linear concentration dependent surface diffusivity, a systematic method is proposed to assess the suitability of use of constant effective surface diffusivity for the uptake of pure gases into a solid sphere. The use of constant effective diffusivities was found to cause a maximum

error of about ten percent.

NOMENCLATURE

C_h : gas phase concentration [mol/m^3]
C_R : reference concentration in gas phase [mol/m^3]
D_h : effective diffusivity at $\theta_h = 0.5$ defined by Eq. (15) [m^2/s]
D_h : (with superscript) diffusivity in each phase [m^2/s]
$D_0{}^s$: surface diffusion coefficient defined by Eq. (13) [m^2/s]
$D_1{}^s$: coefficient used in Eq. (13) [m^2/s]
$D_{h1}{}^{sp}$: coefficient used in Eq. (35) [m^2/s]
$D_h{}^k$: Knudsen diffusion coefficient [m^2/s]
f_h : surface area fraction defined by Eq. (5) [-]
J_h : (with superscript) mass flux in each phase [mol/m^{2}s]
K : equilibrium constant [-]
K_h : effective equilibrium constant defined by Eq. (12) [-]
Kn : Knudsen number [-]
M_W : molecular weight [kg/mol]
N : number of solid particles per unit pellet volume [m^{-3}]
N_h : amount uptaken per unit volume [mol/m^3]
q_h : amount adsorbed per unit apparent volume [mol/m^3]
r_h : radial position [m]
R : (with subscript c or p) radius of a pellet or a particle [m]
R_g : gas constant [8.314 J/mol K]
S_h : surface area per unit volume [m^2/m^3]
T : absolute temperature [K]
t : time [s]
w : a constant used in Eq. (31)

Greek Letters

δ : ratio of dimensionless space time defined by Eq. (24) [-]
ε_h : porosity [-]
η_h : dimensionless distance [-]
φ : dimensionless time defined by Eq. (23) [-]
λ : mean free path of molecules [m]
μ : viscosity [kg/m·s]
ν : dimensionless space time ratio defined by Eq. (25) [-]
θ_h : dimensionless concentration [-]

ρ : a factor defined by Eq. (16) [-]
$\tau_h{}^g$: tortuosity for gas phase [-]

Superscripts
g : gaseous phase
s : surface phase

Subscripts
a : macropore properties
c : solid particle properties
h : a dummy subscript which may be a, i or t
i : micropore properties
k : Knudsen flow
p : pellet properties
t : total properties

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