Nanometer Pore Size Dependence of Intraparticle Diffusion in Silica Gel

Tomomi Sekine and Kiyoharu Nakatani*
Department of Chemistry, University of Tsukuba, Ibaraki 305-8571

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The sorption of rhodamine 6G into single silica gel microparticles possessing pore sizes of 3, 6, 15, and 30 nm was analyzed using single microparticle injection and microabsorption methods. The intraparticle diffusion of the solute was highly influenced by the pore size of the silica gel. The relationship between the intraparticle diffusion coefficient and a hindrance parameter for the diffusion in the pores is discussed on the basis of a pore and surface diffusion model.

Studies of mass-transfer processes in porous microparticles such as silica gel and active carbon are significant for understanding the physical and chemical processes in separation and catalysis materials, natural soils, and so on. Sorption processes are governed by the mass transfer of a solute between the microparticle surface and the surrounding bulk solution phase, adsorption/desorption at the solid/liquid interface, and intraparticle diffusion. The intraparticle diffusion consists of the diffusion of a solute in the pore solution (pore diffusion) and that of the solute adsorbed on the pore walls (surface diffusion).[1–4] Although the intraparticle diffusion coefficient depends on the pore size, the molecular size of the solute, the adsorption isotherm constants, and so on, quantitative analysis based on the pore size dependence of the intraparticle diffusion has been rarely reported because of lack of appropriate experimental techniques. Recently, we have developed a microabsorption technique combined with the microcapillary injection of a single microparticle, by which kinetic analyses of the sorption and desorption processes of dyes proceeding in single microparticles could be analyzed.[5,6] In this study, we discuss the intraparticle diffusion of a dye in silica gel with various pore sizes.

Spherical silica gels (Fuji Silysia Chemistry Co., Inc., CARiACT Q, particle diameter (d); 32–150 µm) with pore diameters (d_p) of 3 (specific surface area $(A_s) = 6.58 \times 10^6\ \mathrm{cm^2/g}$, specific pore volume $(V_p) = 0.42\ \mathrm{cm^3/g}$), 6 ($A_s = 4.51 \times 10^6\ \mathrm{cm^2/g}$, $V_p = 0.84\ \mathrm{cm^3/g}$), 15 ($A_s = 2.09 \times 10^6\ \mathrm{cm^2/g}$, $V_p = 1.25\ \mathrm{cm^3/g}$) and 30 nm ($A_s = 1.15 \times 10^6\ \mathrm{cm^2/g}$, $V_p = 1.2\ \mathrm{cm^3/g}$) were used. A single silica gel microparticle in an aqueous KCl solution (10^{-3}–10^{-1} M, $1\ \mathrm{M} = 1\ \mathrm{mol/dm^3}$) was injected into an aqueous rhodamine 6G (R6G) solution (concentration $(C_w) = 5 \times 10^{-7}$–1×10^{-5} M) containing the same KCl concentration using a microcapillary manipulation/injection method and the absorption spectra of the single microparticle were measured by a microabsorption method at 298 ± 0.5 K.[5,6]

The absorption spectra of R6G in single silica gel microparticles were measured with time (t), as shown in Figure 1. The spectrum shape of the dye in the particle was analogous to that of the dye monomer in water, and was not changed under the present experimental conditions. The absorbance (A) of the dye increased with t and became saturated. The saturated A, corresponding to A at the sorption equilibrium, was directly proportional to d for the same C_w, ionic strength (I) and d_p. If adsorption of the dye proceeds only at the spherical particle surface, the saturated A is independent of d since the amount of the dye per unit surface area is constant, as previously reported.[7] These results indicate that R6G is extracted into the particle interior and the dye concentration in the single particle at the sorption equilibrium ($C_{p,eq}$) is independent of d.[5,6] Using the molar extinction coefficient of R6G in water (ε at 520 nm $= 9.14 \times 10^4\ \mathrm{cm^{-1}\,M^{-1}}$), $C_{p,eq}$ was determined from the Lambert–Beer's law as an optical path length equal to d. At the sorption equilibrium, $C_{p,eq}$ was analyzed on the basis of the Langmuir isotherm: $C_{p,eq} = K_{ads}C_{p,\infty}C_w/(1 + K_{ads}C_w)$, where K_{ads} and $C_{p,\infty}$ are the adsorption/desorption rate constant ratio of R6G ($(1–4) \times 10^5\ \mathrm{M^{-1}}$) and the saturated amount of the dye sorbed in the single particle ($(1–3) \times 10^{-3}$ M), respectively, as a particle volume equal to $(4/3)\pi(d/2)^3$.

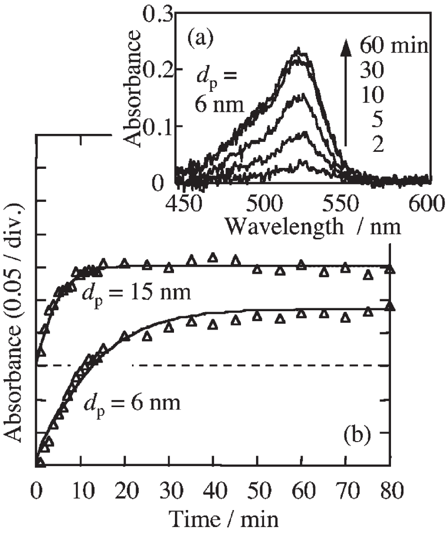

Figure 1. Time dependence of (a) the absorption spectrum of R6G in a single silica gel microparticle for $d_p = 6$ nm ($d = 96$ µm) and (b) the absorbance at 520 nm of R6G in single silica gel microparticles for $d_p = 6$ ($d = 96$ µm) and 15 nm ($d = 98$ µm) at $C_w = 2 \times 10^{-6}$ M and $I = 0.01$. The solid curves in (b) represent the simulations of $A(t)$ by the intraparticle diffusion model ($D_o = 3.5 \times 10^{-9}\ \mathrm{cm^2/s}$ for $d_p = 6$ nm, $D_o = 1.0 \times 10^{-8}\ \mathrm{cm^2/s}$ for $d_p = 15$ nm).

The time dependence of a concentration profile of the dye in the particle ($C_p(r,t)$) is expressed as $\partial C_p(r,t)/\partial t = D_o [\partial^2 C_p(r,t)/\partial r^2 + (2/r)\partial C_p(r,t)/\partial r]$, where r is the radially directed spatial coordinate and D_o is the observed intraparticle diffusion coefficient.[5,6] The initial and boundary conditions were given by $C_p(r,0) = 0$, $C_p(d/2,t) = C_{p,eq}$, and $\partial C_p(0,t)/\partial r = 0$. Thus, the time dependence of A ($A(t) = 2\varepsilon \int_0^{d/2} C_p(r,t)dr$) was simulated by a finite form for various D_o values under the conditions of $\Delta t = 0.5$ s, $\Delta r = 1$ µm, and $D_o\Delta t/(\Delta r)^2 < 0.5$. The observed data were satisfactorily fitted by the simulations

(Figure 1). D_o was independent of d and C_w for the same I and d_p. Therefore, the sorption of R6G into the silica gel can be analyzed on the basis of the intraparticle diffusion model. At $I = 0.01$, the D_o values with d_p values of 3, 6, 15, and 30 nm were determined to be 3.0×10^{-10}, 3.5×10^{-9}, 1.0×10^{-8}, and 1.4×10^{-8} cm^2/s, respectively. As previously reported, D_o increased with increasing I.[6]

According to a pore and surface diffusion model proposed by Ruthven et al., D_o is given by Eq 1.[3,8]

$$D_o = \frac{D_w H(a, d_p)}{\tau_w(1+R)} + \frac{D_s R}{\tau_s(1+R)} \qquad (1)$$

where D_w, D_s, and $H(a, d_p)$ are the diffusion coefficient in the bulk water phase, the surface diffusion coefficient on the pore walls, and the hindrance parameter dependent on the molecular diameter of the solute (a) and d_p, respectively. τ_w or τ_s is the tortuosity for the pore or surface diffusion, respectively. R, defined as the concentration ratio of the solute adsorbed on the pore walls ($C_{p,s}$) to that existing in water in the pores ($C_{p,w}$), is the distribution coefficient in the particle ($R = C_{p,s}/C_{p,w}$). The total concentration of the solute in the particle ($C_{p,eq}$) is the sum of $C_{p,s}$ and $C_{p,w}$ ($C_{p,eq} = C_{p,s} + C_{p,w}$). When $K_{ads}C_w$ is much smaller than unity, the Langmuir isotherm is approximated by $K_{ads}C_{p,\infty} = C_{p,eq}/C_w$. Since C_w is related to $C_{p,w}$ with the porosity of silica gel (ε_p) as $C_w = C_{p,w}/\varepsilon_p$, R is obtained as $R = K_{ads}C_{p,\infty}/\varepsilon_p - 1$, where ε_p is calculated from $\varepsilon_p = V_p/(V_p + \rho_s^{-1})$ and ρ_s is the particle density of silica gel (2.2 g/cm^3).[3] In the present system, R increased with decreasing I and D_o was proportional to $(1+R)^{-1}$ at the same d_p (Figure 2). In Eq 1, the first and second terms correspond to the pore and surface diffusion processes, respectively. The result indicates that the rate-determining step of the intraparticle diffusion is the pore diffusion of R6G.

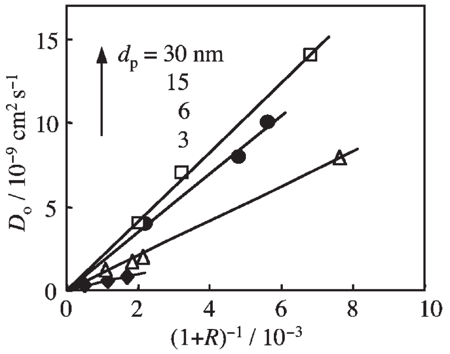

Figure 2. Relationship between D_o and the distribution coefficient for $d_p = 3$ ($I = 0.01$, 0.05, and 0.1), 6 ($I = 0.005$, 0.01, 0.02, and 0.1), 15 ($I = 0.001$, 0.005, and 0.01), and 30 nm ($I = 0.001$, 0.005, and 0.01).

Under the assumption of $D_w/\tau_w = 2.7 \times 10^{-6}$ cm^2/s using $D_w = (4\text{–}6) \times 10^{-6}$ cm^2/s (typical value in water) and $\tau_w = 1.5\text{–}2.3$,[3] $H(a, d_p)$ was determined from the slope of the D_o versus $(1+R)^{-1}$ plot and is summarized in Figure 3. $H(a, d_p)$ is the parameter including the steric and hydrodynamic interactions between the solute and the pore wall. The $H(a, d_p)$ value is in the range of 0–1 and $H(a, d_p) = 1$ means no hindrance. According to the expression reported by Bungay and Brenner, $H(a, d_p)$ is given by Eq 2.[9,10]

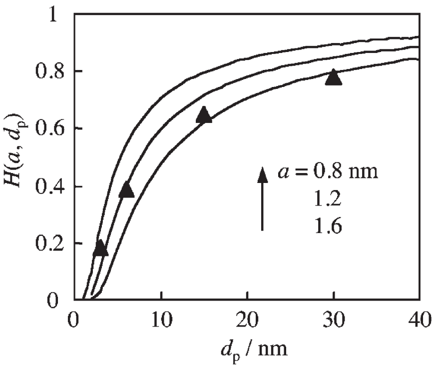

Figure 3. Pore size dependence of $H(a, d_p)$. The solid curves represent the simulations using Eq 2.

$$\begin{aligned} H(a, d_p) = {} & 6\pi(1 - a/d_p)^2/[9/4\pi^2\sqrt{2}(1 - a/d_p)^{-5/2} \\ & \times \{1 - 73/60(1 - a/d_p) + 77293/50400(1 - a/d_p)^2\} \\ & - 22.5083 - 5.6117a/d_p - 0.3363(a/d_p)^2 \\ & - 1.216(a/d_p)^3 + 1.647(a/d_p)^4] \end{aligned} \qquad (2)$$

This equation can be applied in the a/d_p range of 0–1. If a/d_p is smaller than 0.4, the Renkin equation can be used.[10] In the present system, $H(a, d_p)$ was simulated for various a values using Eq 2 (Figure 3). The calculated $H(a, d_p)$ values increased with the decreasing a value at the same d_p. When d_p is much greater than a ($a/d_p \ll 0.04$), the hindrance for the solute diffusion in the pores is negligibly small. The simulated curve at $a = 1.2$ nm agrees very well with the observed $H(a, d_p)$ values. It is noteworthy that the a value of 1.2 nm is close to the actual molecular diameter of R6G. Therefore, the pore diffusion process can be quantitatively analyzed by the present model.

The intraparticle mass-transfer processes of R6G in single silica gel microparticles for various d_p values were investigated by the single microparticle injection and microabsorption methods. The relationship between the observed D_o and d_p could be quantitatively discussed on the basis of the pore diffusion model for the first time. The present approach would be useful to obtain information of diffusion, adsorption/desorption, complexation, and so forth, in the nanometer-sized pores of microparticles.

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References

1 K. Miyabe and G. Guiochon, *Anal. Chem.*, **72**, 5162 (2000).
2 P. Grathwohl, "Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics," Kluwer Academic Publishers, Boston (1998).
3 R. Bujalski and F. F. Cantwell, *Langmuir*, **17**, 7710 (2001).
4 H. Yoshida, M. Yoshikawa, and T. Kataoka, *AIChE J.*, **40**, 2034 (1994).
5 K. Nakatani and T. Sekine, *Langmuir*, **16**, 9256 (2000).
6 T. Sekine and K. Nakatani, *Langmuir*, **18**, 694 (2002).
7 N. Kitamura, M. Hayashi, H.-B. Kim, and K. Nakatani, *Anal. Sci.*, **12**, 49 (1996).
8 D. M. Ruthven, "Principles of Adsorption and Adsorption Processes," Wiley, New York (1984).
9 W. M. Deen, *AIChE J.*, **33**, 1409 (1987).
10 W. M. Deen, C. R. Bridges, B. M. Brenner, and B. D. Myers, *Am. J. Physiol.*, **249**, F374 (1985).