Analysis of Sorption into Single ODS-Silica Gel Microparticles in Acetonitrile–Water

Kiyoharu NAKATANI[†] and Hiroshi KAKIZAKI

Department of Chemistry, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8571, Japan

Intraparticle mass transfer processes of Phenol Blue (PB) in single octadecylsilyl (ODS)-silica gel microparticles in acetonitrile–water were analyzed by microcapillary manipulation and microabsorption methods. An absorption maximum of PB, the sorption isotherm parameters, and the sorption rate in the microparticle system were highly dependent on the percentage of acetonitrile in solution. The results are discussed in terms of the microscopic polarity surrounding PB in the ODS phase and the relationship between the isotherm parameters and the sorption rate.

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Introduction

Studies of the sorption and desorption processes in microparticle systems are significant for understanding the microscopic mechanisms of solid-phase extraction, liquid chromatography, mass transport in soil, and so forth.^{1–8} Because the sorption and desorption processes of a solute in octadecylsilyl (ODS)-silica gel systems are highly dependent on the volume ratio of an organic solvent to water in a mixture solvent, measurements of the microscopic polarity of an ODS phase are necessary for analyses of the separation processes. In liquid chromatography, a solute in a mobile phase distributes into an ODS phase, dependent on the flow rate of the mobile phase, the adsorption/desorption rates, the intraparticle diffusion rate, and so on. Therefore, direct measurements of the sorption rates in ODS-silica gel systems are indispensable for analyzing the separation mechanism. In this article, the sorption of Phenol Blue (PB), known as a solvatochromic dye,⁹ into single ODS-silica gel microparticles in acetonitrile–water was analyzed using microcapillary manipulation and microabsorption methods, by which a single microparticle can be injected into a solution and the absorption spectrum of the single microparticle is measured with time.^{10,11} We discuss the microscopic polarity in the ODS-silica gel system and diffusion of PB in the pores of the microparticles.

Experimental

After spherical ODS-silica gel (Wako Pure Chemical, Wakosil 40C18: particle diameter (d), 20–60 μm ; surface area, 330 cm^2/g ; pore diameter (d_p), 12 nm; pore volume (V_p), 1.0 cm^3/g) was soaked in acetonitrile, the solvent was repeatedly replaced with acetonitrile–water (percentage by volume of acetonitrile, 0–15 vol%) containing KCl (0.01 mol/dm^3). Single microparticle measurements were performed at 298 ± 0.5 K by microcapillary manipulation and microabsorption methods (Fig.

1).^{10,11} A single ODS-silica gel in a KCl/acetonitrile–water solution was sucked into a microcapillary and injected into a KCl (0.01 mol/dm^3)/acetonitrile–water solution containing PB using the microcapillary manipulation method. The time dependence of the absorption spectrum for a single microparticle was measured by the microabsorption method.

Results and Discussion

Figure 2 shows the absorption spectra of PB sorbed into single ODS-silica gel microparticles for 0 and 15 vol% of acetonitrile. The absorbance of PB increased with time and became saturated. Both the ratio of a saturated absorbance value (A_{eq}) to the PB concentration in an acetonitrile–water solution ($C_{\text{a-w}}$) and the time to saturation significantly increased with the decreasing percentage of acetonitrile. The absorption spectrum of PB is highly dependent on the solvent polarity and hydrogen bonding.⁹ In water, acetonitrile (20 vol%)–water, methanol, or acetonitrile, the absorption maximum of PB (λ_{max}) was

Fig. 1 Block diagram of microcapillary manipulation and microabsorption methods.

[†] To whom correspondence should be addressed.
E-mail: nakatani@chem.tsukuba.ac.jp

Fig. 2 Absorption spectra of PB in single ODS-silica gel microparticles for (a) 0 vol% ($C_{a-w} = 3 \times 10^{-7}$ mol/dm³, $d = 45$ μ m) and (b) 15 vol% of acetonitrile ($C_{a-w} = 2 \times 10^{-5}$ mol/dm³, $d = 48$ μ m).

determined to be 658, 648, 609, or 583 nm, respectively. In the ODS-silica gel system, λ_{max} in the single microparticle was 626, 615, 612, or 609 nm for 0, 5, 10, or 15 vol% of acetonitrile, respectively. λ_{max} in the microparticle for 0 vol% of acetonitrile (626 nm) is much smaller than that in water (658 nm). The microscopic polarity surrounding PB is low due to the distribution of PB into the ODS phase. However, λ_{max} in the microparticle is greater than that in acetonitrile (583 nm). Therefore, PB will be located in the vicinity of the ODS/solution interface and be partially solvated by solvent molecules.

Figure 3 shows the time dependence of the PB absorbance ($A(t)$) for 0 vol% of acetonitrile in the microparticle system. A_{eq} was directly proportional to d . A probe beam (2 μ m spot size) from the halogen lamp was passed through the particle center during the microabsorption method (Fig. 1).¹¹ If PB is adsorbed only on the particle surface, A_{eq} is independent of d , as previously reported.¹² This result indicates that water molecules enter the pores having hydrophobic walls in the ODS-silica gel, and PB is sorbed into the particle interior. The PB concentration in the microparticle at sorption equilibrium ($C_{p,eq}$) was determined using Lambert-Beer's law, $A_{eq} = \epsilon d C_{p,eq}$, where ϵ is the molar extinction coefficient of PB at the peak wavelength. Because the respective ϵ values in water and acetonitrile were 2.0×10^4 and 2.1×10^4 mol⁻¹ dm³ cm⁻¹, ϵ in the microparticle was assumed to be equal to be 2.0×10^4 mol⁻¹ dm³ cm⁻¹. We analyzed $C_{p,eq}$ and C_{a-w} using the Langmuir isotherm, $C_{p,eq} = K_L C_{p,\infty} C_{a-w} / (1 + K_L C_{a-w})$, where K_L and $C_{p,\infty}$ are the Langmuir isotherm constant and the Langmuir constant, respectively. C_{a-w} at the sorption equilibrium was assumed to be equal to that at the sample preparation because the volume of the solution phase (3 cm³) was much greater than that of a single microparticle (1.4×10^{-8} cm³ for $d = 30$ μ m). K_L drastically changed with the percentage of acetonitrile (5.3×10^5 (0 vol%), 2.0×10^5 (5 vol%), 1.2×10^4 (10 vol%), 9.3×10^3 mol⁻¹ dm³ (15 vol%)), while $C_{p,\infty}$ was almost constant ($(5 \pm 2) \times 10^{-2}$ mol/dm³).

External mass transfer from a bulk solution phase to a single microparticle surface (spherical diffusion) is much faster than the intraparticle mass transfer, as reported in single silica gel microparticle systems.¹⁰ Therefore, sorption into single microparticles can be analyzed using an intraparticle diffusion

Fig. 3 Time dependence of the peak absorbance of PB in single ODS-silica gel microparticles with $d = 45$ and 21 μ m for 0 vol% of acetonitrile at $C_{a-w} = 3 \times 10^{-7}$ mol/dm³. The solid curves represent the simulations of $A(t)$.

model. For a spherical particle, the time dependence of the radial concentration profile of a solute in the particle ($C_p(r,t)$) is given by the equation $\partial C_p(r,t)/\partial t = D_o \{ \partial^2 C_p(r,t)/\partial r^2 + (2/r) \partial C_p(r,t)/\partial r \}$, where D_o and r are the apparent diffusion coefficient of the solute in the particle interior and the radially directed spatial coordinate, respectively.^{11,13} Under the conditions $C_p(r,0) = 0$, $C_p(d/2,t) = C_{p,eq}$ and $\partial C_p(0,t)/\partial r = 0$, $A(t) (= 2\epsilon \int_0^{d/2} C_p(r,t) dr)$ was simulated for various D_o values. The simulated $A(t)$ curves of single microparticles for 0 vol% of acetonitrile are shown in Fig. 3. The D_o value was independent of C_{a-w} and d for the same percentage of acetonitrile, while D_o increased with the increasing percentage of acetonitrile.

Intraparticle diffusion processes consist of diffusion in a solution phase of pores (pore diffusion) and that at the interface of the pore walls (surface diffusion). The contribution of the surface diffusion to D_o is generally assumed to be negligibly small in silica gel systems. In this case, D_o is given by the equation $D_o = D_{a-w} H(a,d_p) / \tau (1 + K_c)$,¹⁴ where D_{a-w} and τ are the diffusion coefficient of PB in the acetonitrile-water phase and the tortuosity of the ODS-silica gel (1.5),¹⁵ respectively. K_c is the distribution coefficient, defined by the ratio of the PB concentration in the ODS phase at the pore wall ($C_{p,ODS}$) to that in the solution phase in the pores ($C_{p,a-w}$), and is obtained by $K_L C_{p,\infty} / \epsilon_p - 1$ because of $C_{p,eq} = C_{p,ODS} + C_{p,a-w}$ and $C_{a-w} = C_{p,a-w} / \epsilon_p$ (ϵ_p : porosity, 0.69).¹⁵ $H(a,d_p)$ is the hindrance parameter, dependent on the diameter of PB ($a = 1$ nm) and d_p (12 nm), and is estimated to be 0.69 using the Renkin equation: $H(a,d_p) = (1 - a/d_p)^2 \{ 1 - 2.10(a/d_p) + 2.09(a/d_p)^3 - 0.95(a/d_p)^5 \}$.¹⁶ Figure 4 shows the K_c dependence of D_o . A theoretical curve simulates the data at $D_{a-w} = 6 \times 10^{-6}$ cm²/s, which is close to the typical diffusion coefficient of a solute in water. This result indicates that the sorption of PB into the ODS-silica gel can be successfully analyzed by the present theoretical pore diffusion model.

Conclusions

The sorption of PB into ODS-silica gel was sufficiently analyzed by single microparticle measurements. We showed that PB adsorbs at the ODS/solution interface in the pores. Although the pore walls are hydrophobic, water, acetonitrile and PB molecules could enter the particle interior in the ODS-silica gel. The Langmuir isotherm parameters and D_o were highly dependent on the percentage of acetonitrile in solution. On the

Fig. 4 Relationship between the distribution coefficient (K_c) and the apparent diffusion coefficient (D_o) for 0 – 15 vol% of acetonitrile. The solid curve represents the calculation of D_o using $H(a, d_p) = 0.69$, $\tau = 1.5$ and $D_{a-w} = 6 \times 10^{-6} \text{ cm}^2/\text{s}$.

other hand, the relationship between the isotherm parameters and D_o could be analyzed on the basis of the pore diffusion model, independent of the percentage of acetonitrile. We consider that valuable information on microparticles for solid-phase extraction and liquid chromatography can be obtained using the present technique.

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