Notes

Mass Transfer of Water-insoluble Organic Compound from Octadecylsilyl-silica Gel into Water in the Presence of a Nonionic Surfactant

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The release of perylene from octadecylsilyl (ODS)-silica gel into water using a nonionic surfactant was kinetically studied by single microparticle injection and absorption microspectroscopy techniques. The release of perylene from the porous microparticles significantly depended on the surfactant concentration. The release rate constant was inversely proportional to the microparticle radius; the rate-determining step was the process at the spherical microparticle surface. The mechanism is discussed in terms of the solubilization of perylene at the microparticle surface by the micelle.

Introduction

Sorption and release processes of an adsorbate in a porous material/solution system consist of external mass transfer between the material surface and the surrounding solution phase, adsorption/desorption on the material surface and the pore walls, diffusion in the pores, *etc*. In chromatography, solid phase extraction, drug delivery systems, and soil remediation, kinetic analyses of the sorption and release processes are important.[1-14] Surfactants are frequently used in porous material systems. For example, the dissolution of water-insoluble organic compounds from a soil or porous medium has been demonstrated on the basis of the characteristic behavior of surfactants.[15,16] The adsorption and desorption of a water-insoluble organic compound in a porous material are influenced by the surfactant, and micelle formation of the surfactant facilitates solubilization of the adsorbate. Therefore, the kinetic analysis of the mass transfer of a water-insoluble organic compound in a porous material in the presence of a surfactant is significant.

We have reported the sorption or release of an adsorbate for a porous microparticle, such as silica gel and octadecylsilyl (ODS)-silica gel, using the single microparticle measurement technique, by which a single microparticle was injected into a solution and the absorption spectra of the single microparticle were measured.[3,8,10,17] In these systems, the rate-determining step of the sorption or release was the intraparticle diffusion, and the intraparticle diffusion could be discussed on the basis of the pore and surface diffusion model. In the present paper, we report the release of perylene as a water-insoluble organic compound from single ODS-silica gel microparticles into the water phase in the presence of polyoxyethylene (10) octylphenyl ether (Triton X-100). Perylene is only slightly dissolved in water, so perylene sorbed in the ODS-silica gel will not be released from the microparticle into the water phase without Triton X-100. Since perylene and Triton X-100 are nonionic species, the electrostatic interaction can be neglected. Thus, the release process of perylene coupled with the Triton X-100 behavior will be discussed. Furthermore, the pore diameter of the ODS-silica gel used in the present study is comparable to the size of Triton X-100 and the micelle. A kinetic analysis of the mass transfer of these solutes is significant for a fundamental understanding of the physical and chemical processes in the mesopores. We discuss the release mechanism of perylene from the ODS-silica gel into water in the presence of Triton X-100.

Experimental

The spherical ODS-silica gel (Wako Pure Chemical Industries, Wakosil40C18: particle radius (r_p), 10 – 30 μm; surface area, 330 m^2 g^{-1}; pore diameter, 12 nm; pore volume, 1.0 cm^3 g^{-1}) was soaked in *N,N*-dimethylformamide (DMF) and stored for over one day. A small number of ODS-silica gel microparticles in DMF were injected into a DMF/water (weight ratio, 1:1) solution of perylene (1.4×10^{-5} mol dm^{-3}) and left for over one day at 25°C.

For the release measurements of perylene from the ODS-silica gel, a single microparticle in the DMF/water solution was sucked into a microcapillary (tip diameter of ~100 μm) and then injected into an aqueous 10 mmol dm^{-3} potassium chloride solution containing Triton X-100 (0 – 0.1 mol dm^{-3}) of ~15 cm^3 in a glass dish using a microcapillary manipulation/injection system (Narishige, MN-151/IM-16) under an optical microscope (Olympus, IX-70). The absorption spectra of perylene in the single microparticle were measured by an absorption microspectroscopy technique. The experimental setup has already been reported in detail.[3] All single microparticle measurements were performed at 25°C by a temperature controller (Kitazato Supply, MD-10RF-O).

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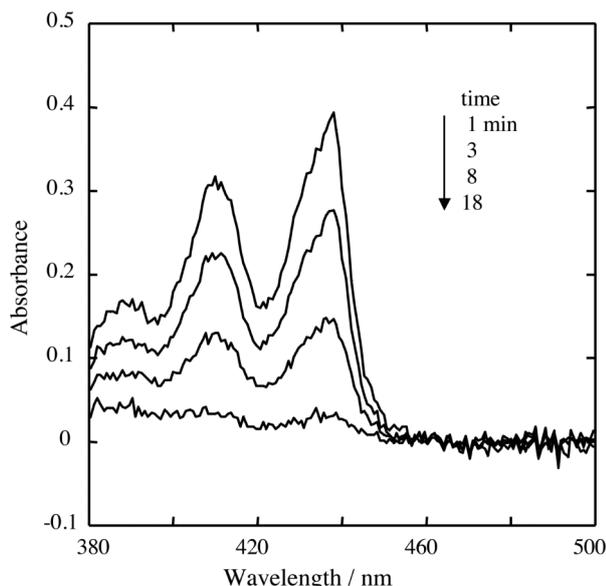E-mail: nakatani@chem.tsukuba.ac.jp

Fig. 1 Time dependence of the absorption spectrum of perylene in a single ODS-silica gel microparticle ($r_p = 27$ μm) injected into an aqueous 60 mmol dm^{-3} Triton X-100 solution.

Fig. 2 Time dependence of absorbance (436 nm) of perylene in single microparticles injected into aqueous Triton X-100 solutions of 0 ($r_p = 24$ μm), 2 ($r_p = 25$ μm), and 60 mmol dm^{-3} ($r_p = 27$ μm). The solid curves represent the values calculated by $A(t) = A_0\exp(-k_{obs}t)$.

Results and Discussion

Perylene was sorbed into the ODS-silica gel in a DMF/water solution. When the absorption spectra of perylene in the ODS-silica gel were measured by the absorption microspectroscopy technique, the absorbance of a single microparticle was directly proportional to r_p, indicating that the perylene molecules are adsorbed into the particle interior.[18] The perylene concentration in the ODS-silica gel was determined to be 1.5×10^{-2} mol dm^{-3} based on the Lambert–Beer law, as the optical length, the molar extinction coefficient (ε), and the volume were assumed to be $2r_p$, 3.9×10^4 cm^{-1} mol^{-1} dm^3 for perylene in cyclohexane, and volume of the sphere ($V = (4/3)\pi r_p^3$), respectively. The ODS-silica gel containing perylene was used for the following release measurements of the perylene from single microparticles.

The release rates of perylene from the single ODS-silica gel microparticles into aqueous solutions in the presence of Triton X-100 were measured. Figure 1 shows the absorption spectra of perylene in a single microparticle ($r_p = 27$ μm) injected into an aqueous 60 mmol dm^{-3} Triton X-100 solution. The absorbance of the perylene decreased with time (t), indicating that the perylene is released from the microparticle. The t dependence of the absorbance at 436 nm ($A(t)$) for various Triton X-100 concentrations is shown in Fig. 2. The release rate of perylene from the microparticle was extremely low in the absence of Triton X-100, while it increased with the increasing Triton X-100 concentration. As a separate experiment, after injection of a single microparticle in the DMF/water solution into an aqueous 10 mmol dm^{-3} potassium chloride solution, the microparticle was allowed to stand for 1 h in the solution. The same microparticle was injected into the 100 mmol dm^{-3} Triton X-100 and 10 mmol dm^{-3} potassium chloride solution and then the release rate of perylene was measured. The release rate was in good agreement with that measured by the direct injection of a microparticle from the DMF/water solution into the 100 mmol dm^{-3} Triton X-100 and 10 mmol dm^{-3} potassium chloride solution. DMF is easily dissolved in water, so that the DMF molecules will rapidly exit from the microparticle into the
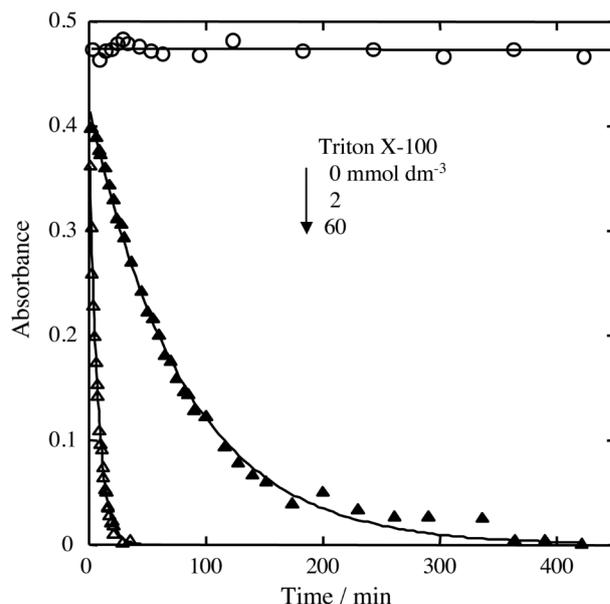
water phase. Therefore, we consider that the release rate of perylene corresponds to the mass transfer of the perylene and/or Triton X-100.

In previous reports, a sorption or release rate of an adsorbate between a porous microparticle and the surrounding solution phase in the absence of a surfactant was limited by the intraparticle diffusion.[8,10,17] As the rate-determining step of the perylene release rate is assumed to be the intraparticle diffusion, the intraparticle diffusion coefficient of perylene or Triton X-100 (D_o) was determined from $A(t)$. The t dependence of the radial concentration profile in the microparticle ($C_p(r,t)$) is given by the spherical diffusion 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 r is the radially directed spatial coordinate. By using an explicit finite differential method, $A(t)$ ($= 2\varepsilon\int_0^{r_p} C_p(r,t)dr$) was simulated for various D_o values. The D_o value should be independent of r_p for the same Triton X-100 concentration conditions.[3] However, the calculated D_o value depended on r_p, although the $A(t)$ curves were reproduced by the simulations. As an example, D_o was determined to be 6.1×10^{-10}, 9.5×10^{-10}, and 1.3×10^{-9} cm^2 s^{-1} for $r_p = 15$, 18, and 27 μm at 30 mmol dm^{-3} Triton X-100, respectively. This result indicates that the release rates cannot be analyzed by the intraparticle diffusion model, and that the intraparticle diffusion is relatively fast.

If the desorption of perylene or the adsorption of Triton X-100 between the pore solution and pore walls (at the solid/solution interface) in the microparticle interior is the rate-determining step for the release of perylene, the time required to $A(t) = 0$ should be independent of r_p. However, the time required to $A(t) = 0$ was significantly influenced by r_p. Therefore, the adsorption/desorption rates of perylene and Triton X-100 at the pore walls are also not the rate-determining steps for the release of perylene.

When the release rate is governed by a process at the spherical microparticle surface, the observed release rate constant (k_{obs}) is given by the equation: $k_{obs} = (S/V)k_s = (3/r_p)k_s$, where S is the surface area ($4\pi r_p^2$) of the spherical microparticle and k_s is the

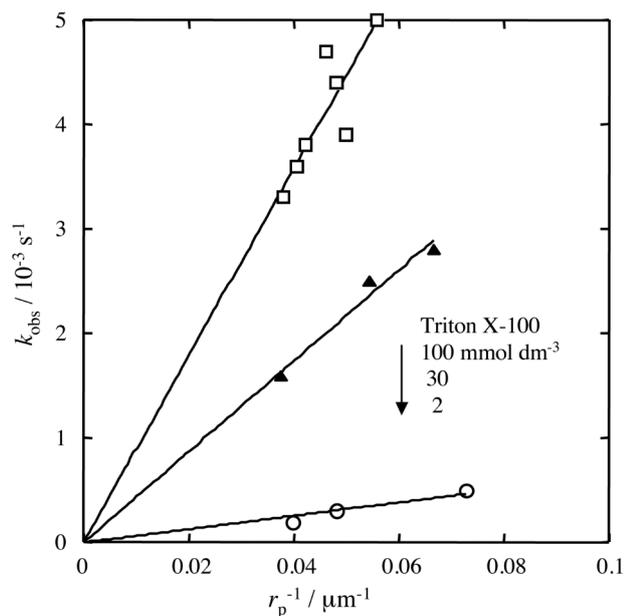Fig. 3 Microparticle size dependence on k_{obs} for 2, 30, and 100 mmol dm^{-3} Triton X-100.

Fig. 4 Triton X-100 concentration dependence on k_s and concentration of perylene dissolved in water.

release rate constant per unit surface area for the sphere.[19,20] Namely, k_{obs} is directly proportional to r_p^{-1}. The observed release rates were then discussed on the basis of this model. $A(t)$ was analyzed based on the first-order reaction type equation: $A(t) = A_0\exp(-k_{obs}t)$, where A_0 is the absorbance at $t = 0$. The observed $A(t)$ curves were thus analyzed by the equation, and we determined the k_{obs} values (Fig. 2). These results are summarized in Fig. 3 as a k_{obs} vs. r_p^{-1} plot. At the same Triton X-100 concentration, k_{obs} was directly proportional to r_p^{-1}. In the present system, the single-microparticle/water volume ratio is so small that the perylene concentration in the water phase is negligibly small even after complete release of the perylene from the single microparticle. Moreover, perylene released from the microparticle efficiently diffuses into the bulk water phase because of the steady-state spherical diffusion in the micrometer-sized particle/solution system.[3] Therefore, the adsorption of perylene from water into the microparticle can be neglected. We consider that the rate-determining step for the release of perylene is a process that occurs at the spherical microparticle surface.

The Triton X-100 concentration dependence of k_s is shown in Fig. 4. k_{obs} could not be calculated at 0 and 0.1 mmol dm^{-3} Triton X-100 since $A(t)$ did not decrease with time (namely, $k_s \sim 0$). k_s was 10^{-9} cm s^{-1} for 0.2 mmol dm^{-3} Triton X-100 and it increased with the increasing Triton X-100 concentration. It is noteworthy that k_s gradually rises from the Triton X-100 concentration near the critical micelle concentration of Triton X-100 (0.2 mmol dm^{-3}).[16] Therefore, the release rate is expected to be influenced by the micelle formation.

The Triton X-100 molecules adsorb on the pore walls. The pore diameter of the ODS-silica gel is 12 nm, while the micelle diameter of Triton X-100 has been reported to be 8.6 nm.[21] Therefore, the micelle would not directly diffuse into the microparticle interior. When the amount of Triton X-100 molecules sorbed in the ODS-silica gel was determined from the Triton X-100 concentration in the aqueous potassium chloride (10 mmol dm^{-3}) solution (30 cm^3) with and without ODS-silica gel (1 g) by conventional absorption spectroscopy,
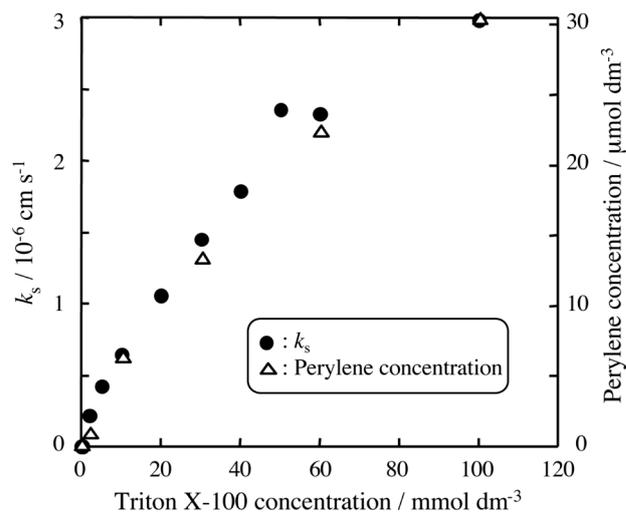
the amount of Triton X-100 molecules in the ODS-silica gel was ~0.5 mmol g^{-1} at a Triton X-100 concentration greater than ~5 mmol dm^{-3} in water. Using the surface area of 330 m^2 g^{-1} for the ODS-silica gel, the amount of Triton X-100 molecules adsorbed on the pore walls of the ODS-silica gel was determined to be 1×10^{-10} mol cm^{-2}, suggesting that the Triton X-100 molecules closely adsorb on the pore walls. Therefore, the intraparticle diffusion, such as the surface diffusion of perylene, will be fast.[4,9] On the other hand, since the micelle formation and dissolution rates for Triton X-100 are much faster than the release rate in the present system,[22] they are also not the rate-determining step for the release of perylene.

The solubility of perylene in water is extremely low. In order to desorb the perylene on the spherical microparticle surface into the water phase, the perylene should enter a micelle in the water phase. As a separate experiment, we measured the solubilization of perylene in the aqueous Triton X-100 solution. An aqueous Triton X-100 solution containing a small amount of perylene powder was shaken (90 rpm) for 24 h and the concentration of perylene dissolved in the water phase was determined (as $\varepsilon = 3.9 \times 10^4$ cm^{-1} mol^{-1} dm^3 for perylene in cyclohexane) by conventional absorption spectroscopy (Fig. 4). It is noteworthy that the shape of the plot of the perylene concentration dissolved in the water phase vs. the Triton X-100 concentration is similar to that of the k_s vs. Triton X-100 concentration plot (Fig. 4). This result indicates that k_s is proportional to the Triton X-100 or the micelle concentration.

Solubilization rate constant values of organic compounds in oil-in-water emulsions using nonionic surfactants have been reported to be $10^{-6} - 10^{-7}$ cm s^{-1},[23] which roughly agree with the k_s values. For the solubilization of water-insoluble oils using nonionic surfactants, the direct detachment of the surfactant micelles at the oil/water interface to move the oil molecules into the aqueous micellar solution has been proposed.[24-26] We consider that k_s is related to such a micelle-mediated solubilization of perylene by Triton X-100 at the microparticle surface.

The release rates of perylene as a water-insoluble organic compound from an ODS-silica gel into water in the presence of Triton X-100 were measured by microcapillary manipulation/injection and absorption microspectroscopy techniques. A large number of Triton X-100 molecules were

adsorbed on the hydrophobic pore walls of the microparticle so that the intraparticle diffusion was relatively fast and was not the rate-determining step of the release rate. We concluded that the release rate is limited by the surface process of the spherical microparticle. The Triton X-100 concentration dependence of k_s was suggested to be due to the solubilization of perylene at the microparticle surface by the micelle.

Acknowledgements

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