Extraction Mechanism of Lanthanide Ions into Silica-based Microparticles Studied by Single Microparticle Manipulation and Microspectroscopy

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Single porous silica microparticles coated with a styrene-divinylbenzene polymer (SDB) impregnated with octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) were injected into an aqueous 3 mol/L nitric acid solution containing trivalent lanthanide (Ln(III)), as a high-level liquid waste model. We used the microcapillary manipulation-injection technique; and the extraction rate of Ln(III), as an Ln(III)-CMPO complex, into the single microparticles was measured by luminescence microspectroscopy. The extraction rate significantly depended on the Ln(III), CMPO, or NO_3^- concentration, and was analyzed in terms of diffusion in the pores of the microparticles and the complex formation of Ln(III). The results indicated that the rate-determining step in Ln(III) extraction was diffusion in the pore solution of the microparticles.

Introduction

In high-level liquid waste for spent nuclear fuels, the separation of trivalent minor actinide (MA(III)) species from solutions containing MA(III), lanthanide (Ln(III)), and so on, is significant for the reduction of radiological risk. Solvent extraction[1,2] and extraction chromatography[3-7] have been proposed as separation methods for MA(III) and Ln(III). In extraction chromatography, as an example, porous silica microparticles coated with styrene-divinylbenzene polymer (SDB) (SiO$_2$-P microparticles) impregnated with organic extractants, such as octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO) (CMPO-SiO$_2$-P microparticles), were used as a stationary phase, and the separation of MA(III) and Ln(III) was demonstrated.[4,8,9] The extraction of Ln(III) by CMPO in a water (w)/oil (o) system was reported to proceed on the basis of Eq. (1):[10-13]

$$Ln^{3+}(w) + 3CMPO(o) + 3NO_3^-(w) \longrightarrow$$
$$Ln(CMPO)_3(NO_3)_3(o). \qquad (1)$$
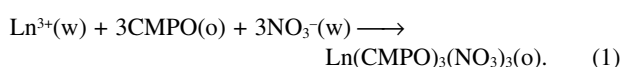
According to extended X-ray absorption fine structure (EXAFS) measurements, Eu(III) has been reported to distribute as Eu(CMPO)$_3$(NO$_3$)$_3$ in CMPO-SiO$_2$-P microparticles.[14]

Kinetic analysis of the extraction and release of MA(III) and Ln(III) in a CMPO-SiO$_2$-P microparticle system is difficult. Various elementary processes, such as the mass transfer of Ln(III) between an aqueous solution and the microparticle surface (external mass transfer), the diffusion of Ln(III) in the pore solution in the particle interior (pore diffusion), and the complex formation reaction between Ln(III) and CMPO, are involved in the extraction of Ln(III) into the CMPO-SiO$_2$-P microparticle system. Although extraction rate measurements are indispensable to mechanistic analysis and speeding-up of separation in extraction chromatography, a detailed kinetic analysis is complicated, and has been scarcely reported for a large number of microparticles in the solution because the external mass transfer depends on the particle-particle distance.

We can measure the extraction rate of a solute from a solution into a microparticle by single microparticle injection and microspectroscopy technique.[15,16] When the single microparticle measurement technique was applied to kinetic analysis of the extraction of Ln(III) into the CMPO-SiO$_2$-P microparticle system, the external mass transfer was rapid, because of efficient three-dimensional diffusion from the bulk solution phase onto the micrometer-sized spherical surface. Therefore, the kinetic analysis was simplified. In this study, the extraction mechanism of Ln(III) from an aqueous 3 mol/L HNO$_3$ solution into a single CMPO-SiO$_2$-P microparticle was investigated, based on kinetic measurements using the single microparticle measurement technique.

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Experimental

Porous silica microparticles (Asahi Kasei, spherical silica particles; particle radius (r): 30 – 35 μm; pore diameter (d_p): 600 nm), CMPO (Katayama Chemical), europium(III) nitrate hexahydrate (Kishida Chemical, 99.9%), neodymium(III) nitrate hexahydrate (Kishida Chemical, 99.9%), samarium(III) nitrate hexahydrate (Kishida Chemical, 99.9%), terbium(III) nitrate hexahydrate (Wako Pure Chemical), 69% nitric acid (Kishida Chemical), and potassium nitrate (Wako Pure Chemical, 99.0%) were used without further purification. Water was purified by deionization and distillation (Yamato Scientific, Auto Still WG203). The surface and pore walls of the porous silica were coated by SDB with a cross-linking degree of 15% (18 wt%) (SiO$_2$-P) by free radical polymerization with a monomer solution containing styrene, divinylbenzene, methyl benzoate, dioctyl phthalate, 2,2′-azobis(iso-butyronitrile), and 1,1′-azobis(cyclo-hexanecarbonitrile), as reported previously.[4,17] CMPO (10 – 20 wt% of the total weight of the SiO$_2$-P) was impregnated in the SDB with acetone, and then the CMPO-SiO$_2$-P microparticles were used after evaporation of the acetone.[17]

The Ln(III) extraction rate was measured using microcapillary manipulation-injection and microspectroscopy, as reported previously.[15,16] A single CMPO-SiO$_2$-P microparticle in an aqueous 3 mol/L HNO$_3$ solution was injected into an aqueous 3 mol/L HNO$_3$ solution (4 mL) containing Ln^{3+} (0.01 – 1.5 mM), using a microcapillary manipulation-injection system (Narishige, MN-151/IM-16), under an optical microscope (Olympus, IX-70); and the rate of Ln(III) extraction into the single microparticle was measured based on the time dependence of the luminescence spectrum of the Ln(III)-CMPO complex. Light beams from a diode laser of 532 nm (Melles Griot, 58gcs405) for Eu(III) and Nd(III), and from a diode laser of 406 nm (NeoArk, TC-20-4030S-2F4.5) for Sm(III), as well as an LED of 480 – 500 nm (BAS, LLS-470 VIS) for Tb(III), were introduced to the optical microscope, and the microparticle was irradiated using an objective lens (Olympus, LUMPLFL60XW). The luminescence from the microparticle was collected by the objective lens and measured by a polychromator (Solar TII, MS2001 I)-multichannel photodetector (Andor Technology, DV401-BV) system. All of the measurements were performed at 296 ± 1 K using a temperature controller (Tokai Hit, MATS-555SNL).

For Langmuir isotherm measurements, a large number of CMPO-SiO$_2$-P microparticles (0.05 – 0.2 g) were dispersed in an aqueous 3 mol/L HNO$_3$ solution (2 – 4 mL) containing Ln^{3+}. The Ln^{3+} concentration in the aqueous solution at the extraction equilibrium ([Ln^{3+}]$_{aq,eq}$) was measured by inductively coupled plasma (ICP) emission spectroscopy (Shimadzu, ICPS-8100). The measurement wavelengths for Eu, Nd, Sm, and Tb were 381.966, 401.225, 359.260, and 350.917 nm, respectively.

The pore size distribution of SiO$_2$-P was analyzed by a surface area and pore size analyzer (Coulter, SA-3100).

Results and Discussion

Microspectroscopy of Eu(III) extraction

A single CMPO-SiO$_2$-P microparticle was injected into an aqueous 3 mol/L HNO$_3$ solution containing Eu^{3+}, and the luminescence from the microparticle was measured. In the present system, luminescence in the bulk solution phase of Eu(III) was not detected. Luminescence of an Ln(III) complex with an appropriate ligand has been reported to be observed.[13] The luminescence spectrum of the Eu(III)-CMPO complex in
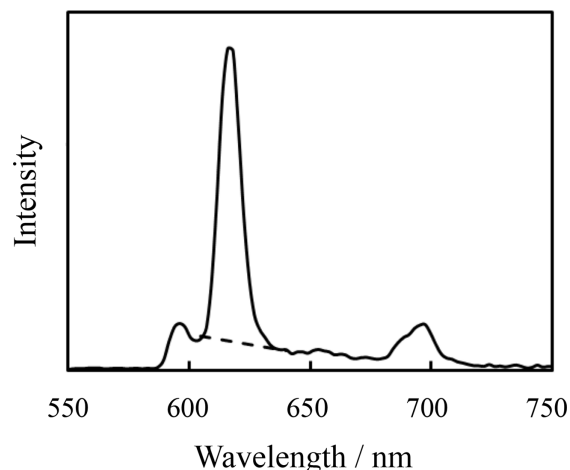

Fig. 1 Luminescence spectrum of an Eu(III)-CMPO complex extracted from an aqueous 3 mol/L HNO$_3$ solution of Eu^{3+} (1 mmol/L) into a single CMPO-SiO$_2$-P microparticle (r = 33.2 μm, 20 wt% CMPO) at the extraction equilibrium.

the single CMPO-SiO$_2$-P microparticle is shown in Fig. 1. To determine the Eu(III) extraction rate, the luminescence intensity at 616 nm ($^5D_0 \rightarrow {}^7F_2$ transition) was measured.[18] Scattered light from the laser beam (532 nm) was strongly observed in the luminescence spectrum from the single CMPO-SiO$_2$-P microparticle, so scattered light of less than ~590 nm was removed by an optical filter. The luminescence intensity at the peak wavelength of around 616 nm was determined by subtracting the intensity of the scattered light as a base line (broken line in Fig. 1).

Figure 2 shows the time (t) dependence of the luminescence intensity for the Eu(III)-CMPO complex at 616 nm ($I(t)$) in single CMPO-SiO$_2$-P microparticles injected into aqueous 3 mol/L HNO$_3$ solutions of various Eu^{3+} concentrations ([Eu^{3+}]$_{aq}$); t was defined as 0 at the moment when the single CMPO-SiO$_2$-P microparticle was injected into the aqueous solution. In the single microparticle/solution system, the change in [Eu^{3+}]$_{aq}$ before and after the extraction of Eu(III) into the single microparticle was negligibly small; and [Eu^{3+}]$_{aq}$ was approximated to [Eu^{3+}]$_{aq,eq}$ because the volume of the single microparticle (1.5×10^{-7} cm^3 for r = 33 μm) was much less than that of the solution (4 mL). $I(t)$ was analyzed by the equation: $I(t) = I_{eq}\{1 - \exp(-k_{ex}t)\}$, where I_{eq} is $I(t)$ at the extraction equilibrium and k_{ex} is the observed extraction rate constant. As shown in Fig. 2, $I(t)$ could be successfully fitted by the first-order reaction rate equation.

Measurements of the dependence of k_{ex} on the Eu^{3+}, CMPO (in particle) or NO$_3^-$ (in aqueous solution, [NO$_3^-$]$_{aq}$) concentration were performed. To analyze the dependence of k_{ex} on [NO$_3^-$]$_{aq}$, KNO$_3$ was added to a 0.01 mol/L HNO$_3$ solution, and the pH of the aqueous solution was maintained at 2.0 to prevent the hydrolysis of Eu^{3+}.[19] k_{ex} was proportional to [Eu^{3+}]$_{aq}$ (Fig. 3), and did not increase with increasing CMPO or NO$_3^-$ concentration (Fig. 4).

The surface area and pore volume (V_p) of SiO$_2$-P were 27.7 m^2/g (BET surface area, correlation coefficient: 0.99995) and 0.543 cm^3/g, respectively. CMPO is dissolved in the SDB layer on the pore walls, and is hardly released from the SDB into the solution phase.[8] CMPO of 20 wt% in the CMPO-SiO$_2$-P microparticle corresponds to 0.49 mol/L (2.7 mol/L in SDB), as the apparent density of the microparticle ($\rho_{app} = (V_p + \rho_s^{-1})^{-1}$
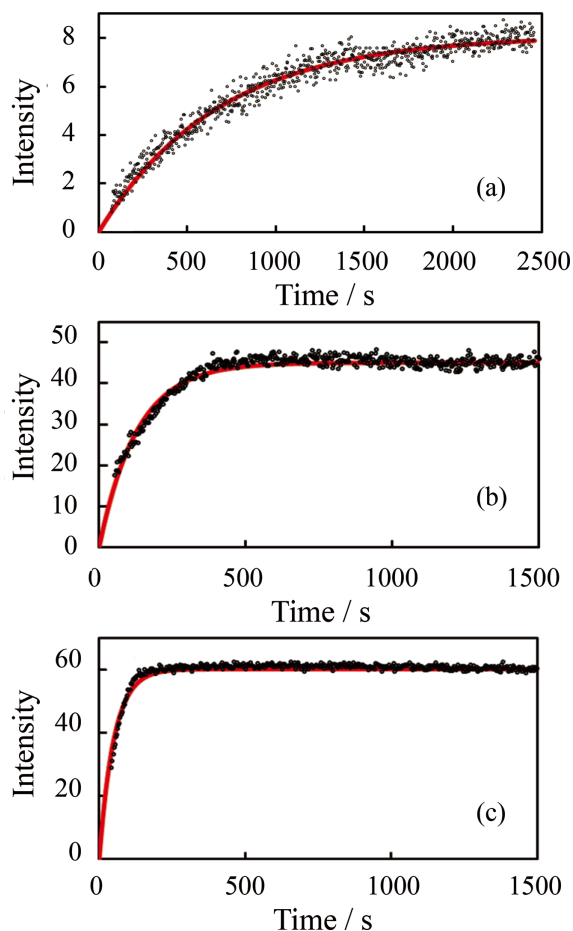
Fig. 2   Time dependence of the luminescence intensity of the Eu(III)-CMPO complex extracted from an aqueous 3 mol/L HNO₃ solution containing Eu³⁺ of (a) 0.01 (r = 33.2 μm), (b) 0.5 (r = 34.0 μm), or (c) 1.5 mmol/L (r = 33.2 μm), into a single CMPO-SiO₂-P microparticle (20 wt% CMPO). The solid curves represent the results of calculations using the first-order reaction rate equation as k_{ex} = (a) 1.5×10^{-3}, (b) 7.7×10^{-3}, and 2.0×10^{-2} s⁻¹.
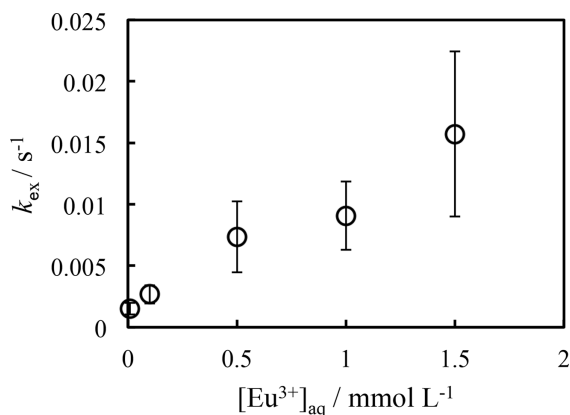

Fig. 3   [Eu³⁺]$_{aq}$ dependence of k_{ex} in the single CMPO-SiO₂-P microparticle/solution system with r = 31.5 – 34.0 μm, 20 wt% CMPO, and 3 mol/L HNO₃.

Fig. 4 k_{ex} for various (a) CMPO (r = 31.5 – 33.2 μm, 3 mol/L HNO₃) and (b) NO₃⁻ (r = 32.3 – 34.0 μm, 0.01 mol/L HNO₃, 20 wt% CMPO) concentrations in the single CMPO-SiO₂-P microparticle/solution system with [Eu³⁺]$_{aq}$ = 1 mmol/L.

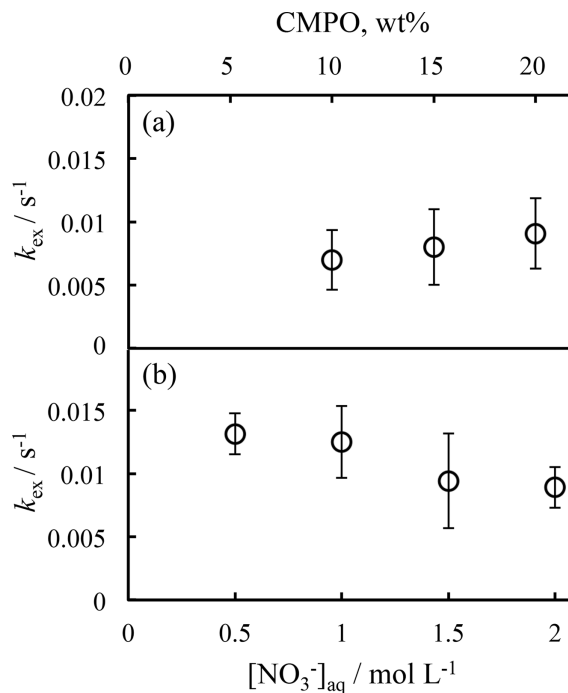(ρ_s, density of silica without pores (2.2 g/cm³))[20] is 1.0 g/cm³. k_{ex} did not increase with increasing CMPO or NO₃⁻ concentration (Fig. 4) so that the complex formation of Eu(III) with CMPO or NO₃⁻ is not the rate-determining step of the extraction rate. Indeed, the ligand exchange reaction of CMPO in solution was reported to be fast (10^3 – 10^4 s⁻¹).[11,21,22]

Intraparticle diffusion

The pore wall of the microparticle was here coated by an SDB layer of several hundred nanometers in depth.[14] The distribution of d_p for SiO₂-P, determined by the BJH desorption method, was <16 nm (0.43%), 16 – 20 nm (1.01%), 20 – 80 nm (84.84%) and >80 nm (13.73%). Therefore, the extraction rates of Ln(III) into the porous microparticles are expected to be limited by intraparticle diffusion. The intraparticle diffusion coefficient (D_p) in the CMPO-SiO₂-P microparticle was experimentally determined by Eq. (2),[23] using r = 33 μm:

$$k_{ex} = \frac{\pi^2 D_p}{r^2}. \tag{2}$$

Intraparticle diffusion in porous silica gel and ODS silica gel consists of diffusion in the pore solution (pore diffusion) and that on the pore walls (surface diffusion), and has been analyzed on the basis of the pore and surface diffusion model.[24–29] When the distribution ratio of Ln(III) between the solution and the microparticle (R) is large (>>1), the intraparticle diffusion coefficient (D_p) is given by Eq. (3),[20,24,27]

$$D_p = \frac{D_w H}{\tau_p\{1 + (R/\varepsilon_p)\}} + \frac{D_s}{\tau_s}, \tag{3}$$

where D_w and D_s are the diffusion coefficient in the bulk water phase and the surface diffusion coefficient, respectively; ε_p is the microparticle porosity and was calculated to be 0.54 from $\varepsilon_p = V_p/(V_p + \rho_s^{-1})$.[20] Further, τ_p or τ_s is the tortuosity for the
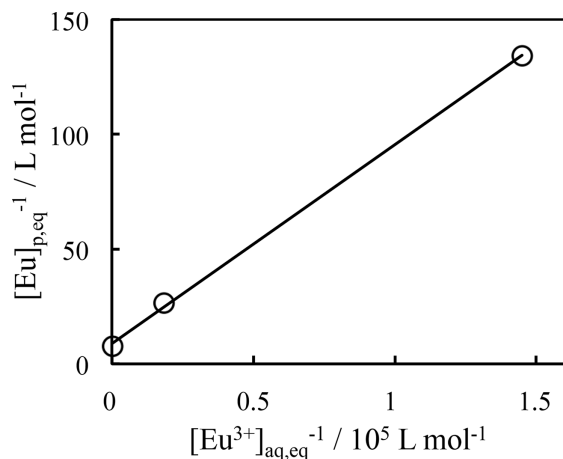
Fig. 5 Langmuir isotherm of Eu(III) in the CMPO-SiO$_2$-P microparticle/solution system with 20 wt% CMPO and 3 mol/L HNO$_3$.

Table 1   Langmuir isotherm parameters of Nd(III), Sm(III), Eu(III), and Tb(III) in the CMPO-SiO$_2$-P microparticle/solution system with 20 wt% CMPO and 3 mol/L HNO$_3$

Ln(III)	K_L/L mol^{-1}	$[Ln]_{p,L}$/mol L^{-1}
Nd(III)	1.9×10^4	0.10
Sm(III)	1.6×10^4	0.11
Eu(III)	1.0×10^4	0.11
Tb(III)	7.9×10^3	0.12

pore or surface diffusion, respectively (1.5 – 2.3 for silica gel).[20] H is the hindrance parameter ($0 < H < 1$), depending on the Ln^{3+} diameter (a, 0.22 nm for Eu(H$_2$O)$_9{}^{3+}$)[30] and d_p, and is given by the Renkin equation (Eq. (4)),[31]

$$H = \{1 - (a/d_p)^2\}\{1 - 2.10(a/d_p) + 2.09(a/d_p)^3 - 0.95(a/d_p)^5\}. \qquad (4)$$

H was calculated to be ~1 for d_p >20 nm (0.96 for d_p = 20 nm, 0.98 for d_p = 50 nm as a = 0.22 nm). In Eq. (3), the first and second terms correspond to the pore and surface diffusion, respectively.

R (= $[Ln]_{p,eq}/[Ln^{3+}]_{aq,eq}$) was here estimated from the Langmuir isotherm equation,

$$\frac{[Ln]_{p,eq}}{[Ln^{3+}]_{aq,eq}} = \frac{K_L[Ln]_{p,L}}{1 + K_L[Ln^{3+}]_{aq,eq}}, \qquad (5)$$

where K_L is the Langmuir isotherm constant. $[Ln]_{p,eq}$ and $[Ln]_{p,L}$ are the Ln(III) concentration at the extraction equilibrium and the saturated amount of Ln(III) in the CMPO-SiO$_2$-P microparticles as ρ_{app} = 1.0 g/cm^3, respectively. Figure 5 shows the Langmuir isotherm for CMPO-SiO$_2$-P microparticles with 20 wt% CMPO (in 3 mol/L HNO$_3$). The Langmuir isotherm parameters for Ln(III) are summarized in Table 1. Since the CMPO molecules in the SDB layer were fixed as reaction sites for complex formation, the extraction of Ln(III) could be analyzed on the basis of the Langmuir isotherm equation. Under the present experimental conditions, R decreased with increasing $[Ln^{3+}]_{aq,eq}$. For the distribution of a dye in a silica-gel system, since any change in the distribution ratio was small for the various dye concentrations in solution, the intraparticle diffusion
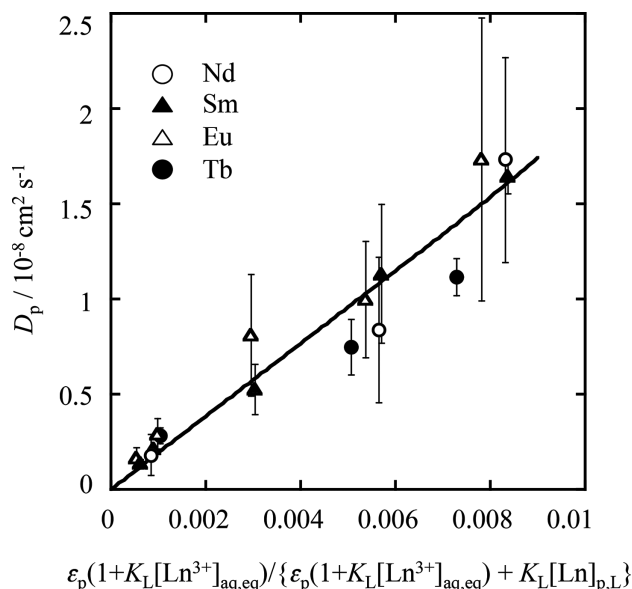

Fig. 6 $\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq})/\{\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq}) + K_L[Ln]_{p,L}\}$ (Ln = Nd, Sm, Eu, and Tb) dependence of D_p in the single CMPO-SiO$_2$-P microparticle/solution system with r = 31.5 – 34.0 μm, 20 wt% CMPO, and 3 mol/L HNO$_3$.

coefficient of the dye was independent of the dye concentration in solution.[15,32]   In the present system, however, R highly depended on $[Ln^{3+}]_{aq,eq}$ and D_p (k_{ex}) was influenced by $[Ln^{3+}]_{aq,eq}$. Therefore, D_p should be expressed in Eq. (6) through Eqs. (3) and (5),

$$D_p = \frac{D_w H \varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq})}{\tau_p\{\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq}) + K_L[Ln]_{p,L}\}} + \frac{D_s}{\tau_s}. \qquad (6)$$

D_p was analyzed on the basis of Eq. (6). As shown in Fig. 6, D_p for Nd(III), Sm(III), Eu(III), and Tb(III) was directly proportional to $\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq})/\{\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq}) + K_L[Ln]_{p,L}\}$. From the slope of the D_p vs. $\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq})/\{\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq}) + K_L[Ln]_{p,L}\}$ plot (Fig. 6), $D_w H/\tau_p$ was determined to be 2×10^{-6} cm^2/s. Using H = 1 and τ_p = 2, D_w is estimated to be 4×10^{-6} cm^2/s, which is in good agreement with D_w reported for Ln(III) in an aqueous solution (($4 – 6) \times 10^{-6}$ cm^2/s).[33] On the other hand, the surface diffusion term, (D_s/τ_s), corresponding to the intercept value of the plot, was negligibly small. The contribution of the surface diffusion of hydrophilic Ln^{3+} along the hydrophobic SDB surface without a reaction between Ln^{3+} and CMPO, to the intraparticle diffusion, will be neglected. From these results, we consider that the extraction rates of Ln(III) are limited by the pore diffusion in the CMPO-SiO$_2$-P microparticle. In the present system, $\varepsilon_p(1 + K_L[Ln^{3+}]_{aq,eq})$ is much smaller than $K_L[Ln]_{p,L}$ and the surface-diffusion term is neglected, so Eq. (6) is approximated to

$$D_p = \frac{D_w H \varepsilon_p}{\tau_p K_L[Ln]_{p,L}} (1 + K_L[Ln^{3+}]_{aq,eq}). \qquad (7)$$

Therefore, D_p, namely, k_{ex} ((Eq. (2)) was proportional to $[Ln^{3+}]_{aq,eq}$, as shown in Fig. 3.

Conclusions

The extraction of Ln(III) into CMPO-SiO$_2$-P microparticles was kinetically analyzed using the single microparticle measurement technique. The extraction rate was governed by the intraparticle diffusion in the CMPO-SiO$_2$-P microparticle. The characteristic [Ln^{3+}]$_{aq}$ dependence of D_p could be analyzed by Eq. (6), and the rate-determining factor was the pore diffusion of Ln^{3+}. Mechanistic analysis of complex formation extraction in a complicated porous particle system was here performed using the single microparticle measurement technique.

Acknowledgements

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