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EXTRACTION OF PALLADIUM(II) WITH THROUGH-HOLE TYPE MICROCAPSULES CONTAINING TRIOCTYLAMINE

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ABSTRACT

Large-diameter and through-hole type microcapsule with entrapped trioctylamine (TOA) as an extractant were prepared by (W/O/W) emulsification and in-situ polymerization method. The morphologies of the microcapsules, their encapsulation efficiencies for TOA, and their forward and back extraction properties for palladium(II) were investigated. The microcapsules ranged in size from 210-420 μm. The encapsulation efficiency of TOA was approximately 100% for all the microcapsules, which indicates minimal loss of TOA during preparation of the microcapsules. Through-hole type microcapsules were obtained when inner aqueous phase contained a high concentration of sodium chloride, and at a moderate agitation speed in the first emulsification. With the through-hole type microcapsules the extraction equilibrium approached one, and the extraction rate was very high compared to other preparation conditions and (O/W) type microcapsules.

Keywords: extraction, palladium, trioctylamine, microcapsules, through-hole

INTRODUCTION

Compared to base metals, precious metals such as chromium, vanadium, gold, and platinum have different characteristics, which facilitate their application as semi-conductors, decorative materials, dental materials, and industrial catalysts. Due to rapid progress in advanced technologies and a rise in aware-

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ness about environmental issues, it is expected that the demand for precious metals as semi-conductors and catalytic converters will increase. Precious metals are produced in limited amounts, difficult to purify because of their chemical properties, and problematic to source due to political unrest in some of the metal-producing countries. This means they are extremely expensive and their supply is very unstable. Stable supply of these valuable metals requires minimization of their waste, and consequently an effective recovery technique needs to be developed. Liquid-liquid extraction has been used for recovery of metals from aqueous solution [1-3]. This method has several advantages, such as high selectivity for a diverse range of metal ions, ability to treat large volumes of wastewater, and scalability. However, it uses large volumes of organic solvent, which could be a concern for the environment and human health. In addition, treatment of effluents with liquid-liquid extraction and regeneration of the extractant can be complicated by emulsification of the organic and aqueous phases. Therefore, alternative extraction methods have been proposed, including extractions with ion-exchange resin [4], solvent impregnated resin [5, 6], supported liquid membranes [7-9] and microcapsules [10-12]. We have investigated the use of microcapsules containing trioctylamine for extraction of palladium(II), Pd(II) from hydrochloric acid [13-15]. Microcapsules are an effective extraction media for Pd(II), and we found when their average diameter decreased (< 20 μm), their extraction rate drastically increased. However, small diameter microcapsules create dust, which can block pipes and be inhaled by humans. In this study, we attempted to prepare through-hole type microcapsules with large diameters. Extraction of Pd(II) with these microcapsules was investigated.

EXPERIMENTAL

Materials

Divinylbenzene (DVB) and styrene were obtained from Wako Pure Chemicals Industries and washed with 10 wt% NaOH to remove the polymerization inhibitor. Trioctylamine (TOA), toluene, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN), hexaglycerol ricinoleic acid (818SX), polyvinyl alcohol (PVA), sodium dodecyl sulfate (SDS), hydrochloric acid, ethanol, butanol, Pd(II) chloride and sodium chloride were also purchased from Wako Pure Chemicals Industries and used without further purification.

PROCEDURES

Preparation of microcapsules containing TOA

The inner aqueous phase was a set concentration of aqueous NaCl. The organic phase included TOA as extractant, DVB and styrene to form the wall of the microcapsules, 818SX as a surfactant, toluene as diluent, and ADVN as initiator. PVA (2 wt% and 0.25 wt% in SDS) was used as the outer aqueous phase. The inner aqueous phase was poured into the organic phase and stirred

using a homogenizer, which produced a (W/O) emulsion. The (W/O) emulsion was poured into the outer aqueous phase to prepare a (W/O/W) emulsion. In-situ polymerization was induced by increasing the temperature to 343 K and stirring at 250 rpm under a nitrogen atmosphere for 5 hours. Through-hole type microcapsules containing TOA were obtained by filtration, washed with distilled water, and dried under vacuum.

MEASUREMENT OF MICROCAPSULE PROPERTIES

The prepared microcapsules ranged in size from 210–420 μm by the classification. The encapsulation efficiency of TOA (E) and the amount of encapsulated TOA per 1 g of microcapsules (E') were measured using the following procedures. First, the TOA in the microcapsules was Soxhlet extracted with ethanol. Then the amount of TOA was determined using a neutralization titration with 0.1 M HCl in a mixture of methanol and butanol. After elution of TOA, the average pore diameter of the microcapsules (D_P) was measured by a Micromeritics Automated Mercury Porosimeter (AutoPore9500, Shimadzu).

FORWARD EXTRACTION OF Pd(II) FROM HYDROCHLORIC ACID SOLUTION

The microcapsules were pre-treated by shaking in 2 M HCl at 150 rpm and 298 K for 24 hours. The solution was then filtered to obtain microcapsules containing TOA · HCl salt, and these were dried under vacuum. The extraction of Pd(II) was investigated by dispersing the pre-treated microcapsules into 0.1 M HCl solutions containing set amounts of $PdCl_2$ by shaking at 150 rpm and 298 K for a prescribed time. The concentration of Pd(II) was assumed to be half of the TOA concentration in the microcapsules from the equation (2). The solution was then filtrated and the concentration of residual Pd(II) in the solution was measured using inductively coupled plasma spectrometry (ICP, IRIS Advantage, Nippon Jarrell-Ash). The extraction equilibrium equations are shown below.

$$\mathrm{TOA + HCl \leftrightarrow TOA \cdot HCl} \tag{1}$$

$$\mathrm{2(TOA \cdot HCl) + PdCl_4^{2-} \leftrightarrow (TOA \cdot HCl)_2 \cdot PdCl_2 + 2Cl^-} \tag{2}$$

The forward extraction ratio (E_f) and the initial forward extraction rate (R_f) are defined as follows:

$$E_f = \frac{\left(C_{Pd,sol,ini} - C_{Pd,sol}\right) \cdot V_{sol} / M_{MC}}{E'/2} = \frac{C_{Pd,ext,MC}}{E'/2} \text{ [-]} \tag{3}$$

$$R_f = \frac{C_{Pd,ext,MC,\Delta t}}{\Delta t} \text{ [mmol/g·s]} \tag{4}$$

BACK EXTRACTION OF Pd(II) FROM MICROCAPSULES

Microcapsules pretreated with HCl were dispersed into 0.1 M HCl solutions containing an excess of $PdCl_2$ and shaken at 150 rpm for 24 hours. After filtration and drying under vacuum, microcapsules containing Pd(II) complexes were obtained. These microcapsules were placed in 10 mM thiourea in 0.1 M HCl, and back extraction was carried out with shaking at 150 rpm and 298 K for a set time. Finally, the concentration of eluted Pd(II) was measured using ICP. The back extraction ratio (E_b) is defined as follows:

$$E_b = \frac{C_{Pd,elu,sol} \cdot V_{sol}}{C_{Pd,MC,ini} \cdot M_{MC}} \text{ [-]} \quad (5)$$

RESULTS AND DISCUSSION

Effect of experimental conditions on microcapsule morphology

We investigated the effects of different experimental conditions on the formation of through-hole type microcapsules. Figure 1 shows the SEM images of microcapsules prepared with various sodium chloride concentrations in the inner aqueous phase, and using different agitation speeds for the first emulsification (Fig. 2).

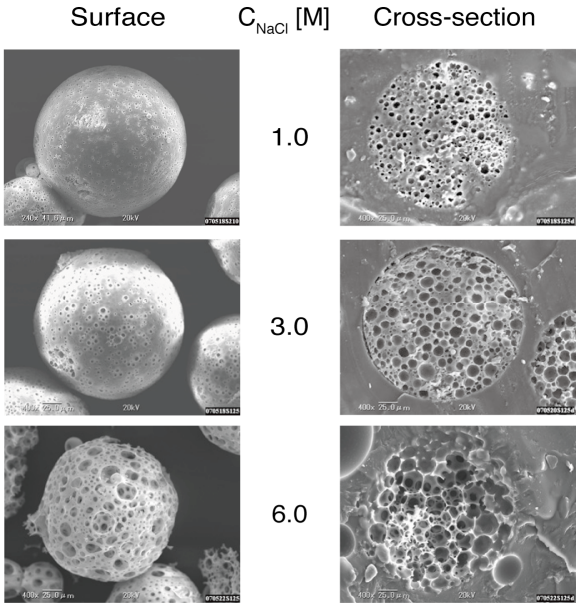

Fig. 1. SEM images of microcapsules prepared with various sodium chloride concentrations in the inner aqueous phase.

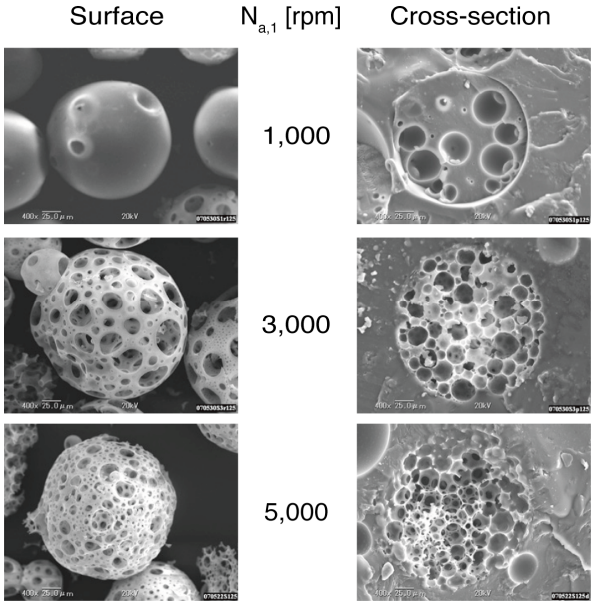

Fig. 2. SEM images of microcapsules prepared with various agitation speeds during the first emulsification.

The diameter of surface and internal pores increased with an increase of sodium chloride concentration. With high sodium chloride concentration, water in the outer aqueous phase moved into the inner aqueous phase by osmosis, and aqueous droplets in the inner phase enlarged and aggregated. This created large surface and internal pores and resulted in the formation of through-hole type microcapsules. With the agitation speed, a moderate speed (3,000 rpm) appeared to give the best through-hole type structure. At an agitation speed of 1,000 rpm the inner aqueous droplets were too large and unstable, which resulted in rupture of the droplets into the outer aqueous phase and reduction of the number of internal pores. Increasing the agitation speed stabilized the large aqueous droplets and through-hole type microcapsules formed.

Figure 3 shows the effects of sodium chloride concentration and Figure 4 shows the agitation speed on the average pore diameter and pore volume of the microcapsules were also investigated. In these figures, the peak at around 10^5 nm arises from the spaces between individual microcapsules. The through-hole type microcapsules had a sharp peak at around 10 μm (Figs. 3 and 4), which corresponds to the size of the pores observed by SEM observation. These results suggest the surface and internal pores have diameters of around 10 μm.

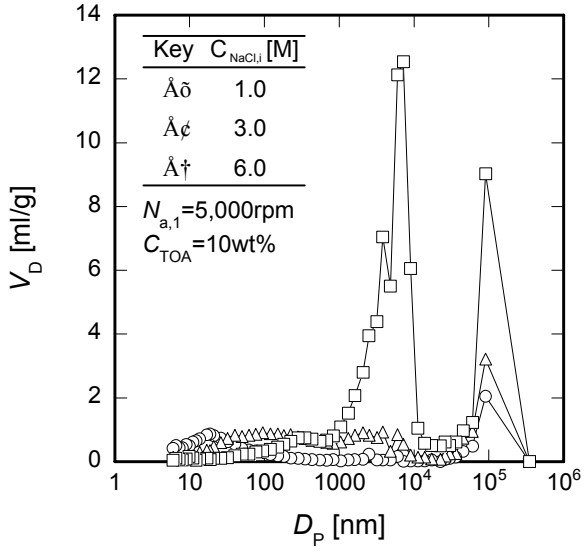

Fig. 3. Effect of sodium chloride concentration on the pore distribution of microcapsules.

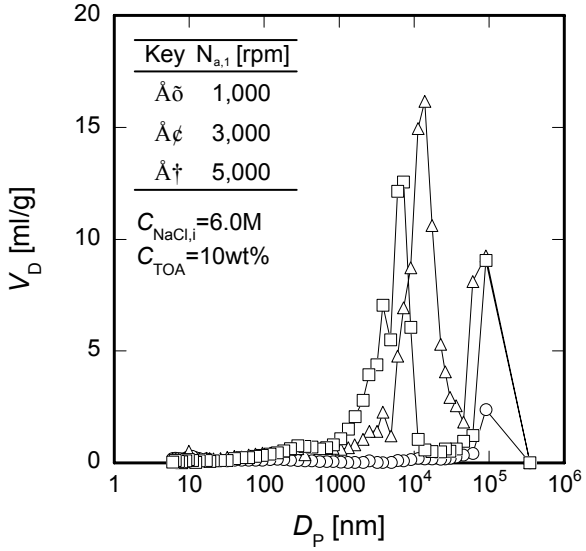

Fig. 4. Effect of agitation speed on the pore distribution of microcapsules.

FORWARD EXTRACTION OF Pd(II) USING THE MICROCAPSULES

Previously, we investigated the extraction of Pd(II) using (O/W) type microcapsules [15]. The extraction of Pd(II) using (O/W) type microcapsules involved an initial extraction step, an internal diffusion step, and an extraction equilibrium step. Among these extraction steps, internal diffusion is rate-controlling step. Therefore, it is very important to shorten the internal diffusion

distance, and extraction from the inside and outside of the microcapsule appeared to be an effective way to achieve this. The effect of sodium chloride concentration in the inner aqueous phase on the forward extraction of Pd(II) (Fig. 5) and on the initial forward extraction rate (Fig. 6) was investigated. The extraction ratio approached one when the sodium chloride concentration was 6.0 M, which indicates almost complete extraction of Pd(II). The initial extraction rate increased with increasing sodium chloride concentration.

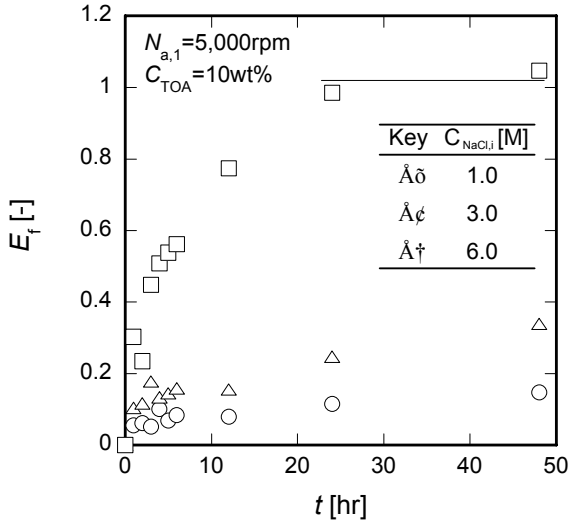

Fig. 5. Effect of sodium chloride concentration in the inner aqueous phase on the forward extraction of Pd(II).

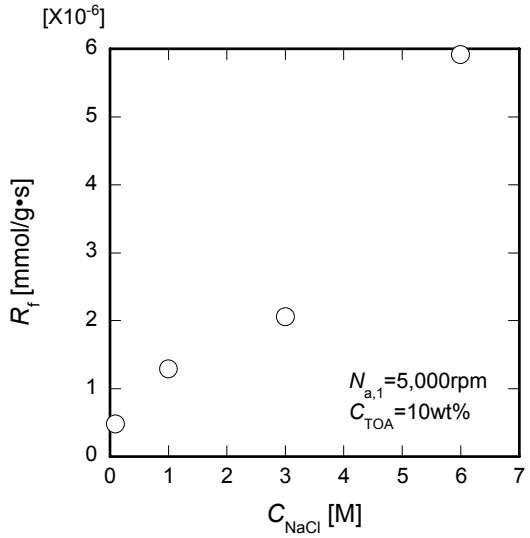

Fig. 6. Effect of sodium chloride concentration in the inner aqueous phase on the initial forward extraction rate.

The effect of agitation speed on the forward extraction of Pd(II) (Fig. 7), and on the forward extraction rate of Pd(II) (Fig. 8) was also investigated. With an agitation speed of 3,000 rpm, the extraction rate was very high compared to extraction with the other agitation speeds investigated. As discussed earlier, microcapsules prepared at 3,000 rpm have large surface and internal pores. These pores facilitate the increase in forward extraction ratio and forward initial extraction rate compared to extractions at other agitation speeds. Finally, we attempted to increase the initial extraction rate by changing the TOA concentration.

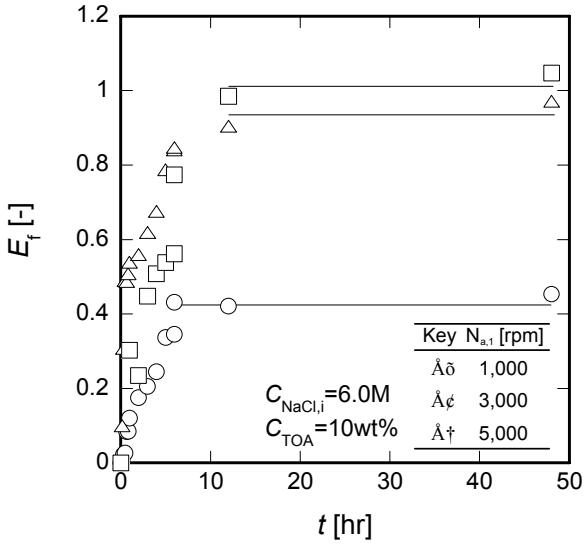

Fig. 7. Effect of agitation speed on the forward extraction of Pd(II).

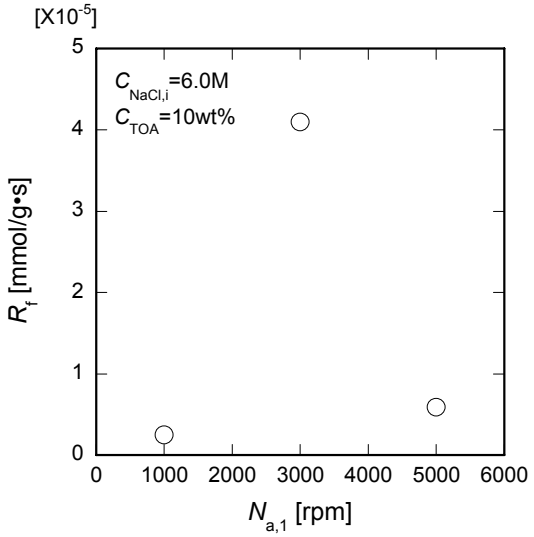

Fig. 8. Effect of agitation speed on the initial forward extraction rate of Pd(II).

Figure 9 and Figure 10 show the effect of TOA concentration on forward extraction of Pd(II) and the forward extraction rate, respectively. At all TOA concentrations the through-hole type microcapsules reached high forward extraction ratios over time. However, the initial forward extraction rate was drastically increased with increasing TOA content in the microcapsules.

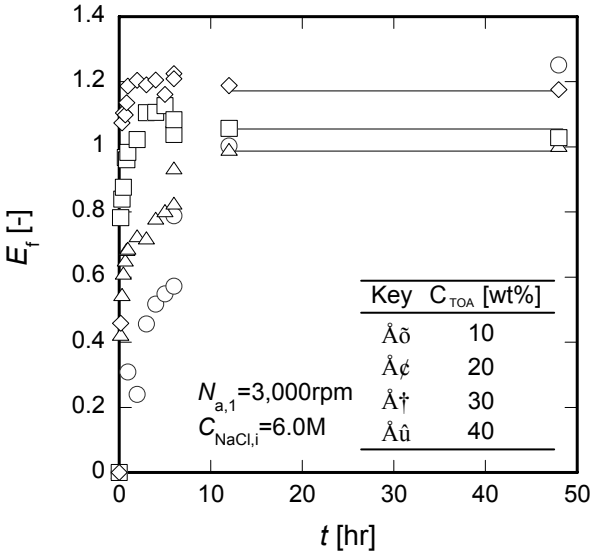

Fig. 9. Effect of TOA concentration on the forward extraction of Pd(II).

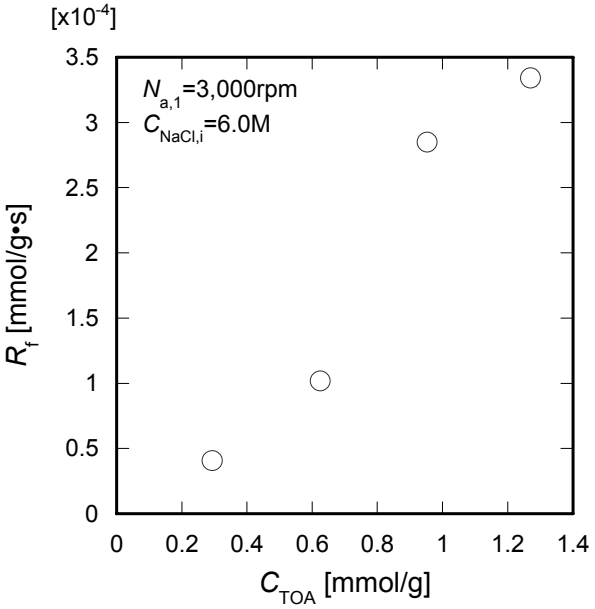

Fig. 10. Effect of TOA concentration on the initial forward extraction rate of Pd(II).

BACK EXTRACTION OF Pd(II) FROM THROUGH-HOLE TYPE MICROCAPSULES

Back extraction of Pd(II) from the through-hole type microcapsules was investigated at various DVB concentrations as shown in Figure 11. The time taken for the back extraction to reach completion, which is indicated by a back extraction ratio of one, was relatively short. With a high DVB concentration, the back extraction reached completion more rapidly than with a low DVB concentration. This was caused by an increase in microcapsule surface area at higher DVB concentrations as shown in Figure 12.

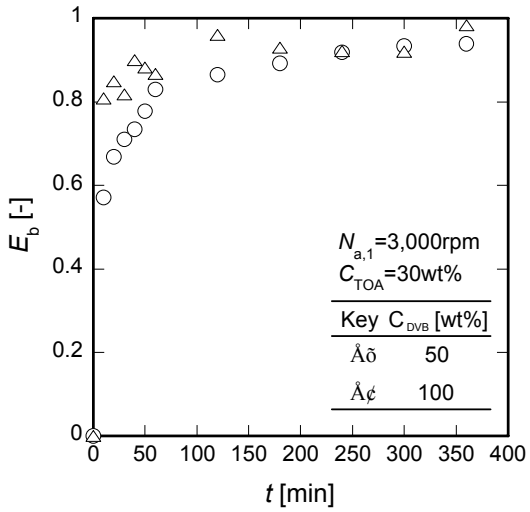

Fig. 11. Effect of DVB concentration on the back extraction of Pd(II) from the through-hole type microcapsules.

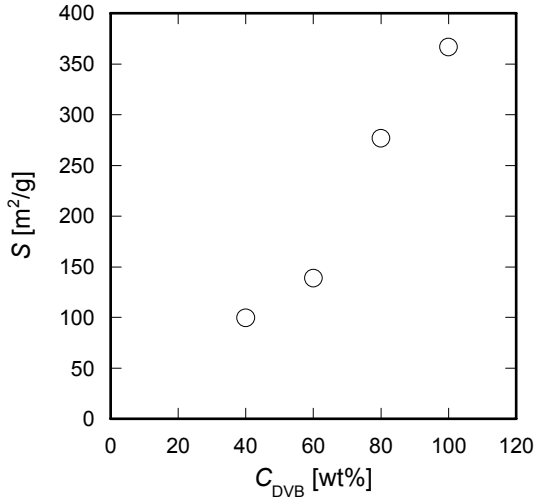

Fig. 12. Effect of DVB concentration on the surface area of the microcapsules.

CONCLUSIONS

Through-hole type microcapsules with large diameters and containing TOA as an extractant were prepared using (W/O/W) emulsification and in-situ polymerization. The morphologies of the microcapsules, encapsulation efficiencies of TOA, and their performance for forward and back extraction of Pd(II) were investigated. The following results were obtained:

1. Through-hole type microcapsules were prepared when the inner aqueous phase contained a high concentration of sodium chloride, and at a moderate agitation speed in the first emulsification.
2. The forward extraction was completed only using the through-hole type microcapsules.
3. The initial extraction rate drastically increased with a higher TOA content in the microcapsules.
4. The through-hole type microcapsules and high TOA content were effective for extraction of Pd(II).
5. The back extraction was completed in a short time and had a high extraction ratio.

ACKNOWLEDGMENT

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LIST OF SYMBOLS

C_{DVB} – divinylbenzene concentration in organic phase [wt%],
$C_{Pd,elu,sol}$ – Pd(II) concentration in aqueous solution after back extraction experiment [mmol/dm^3],
$C_{Pd,ext,MC}$ – Pd(II) concentration in microcapsules after forward extraction experiment [mmol/g],
$C_{Pd,ext,MC,\Delta t}$ – Pd(II) concentration in microcapsules at initial forward extraction [mmol/g],
$C_{Pd,MC,ini}$ – initial Pd(II) concentration in microcapsules [mmol/g],
$C_{Pd,sol,\ ini}$ – initial Pd(II) concentration in aqueous solution [mmol/dm^3],
$C_{Pd,sol}$ – Pd(II) concentration in aqueous solution after forward extraction [mmol/dm^3],
C_{TOA} – trioctylamine concentration in organic phase [wt%],
D_p – average pore diameter of microcapsules [nm],
E' – TOA content in the microcapsules [mmol/g],
E_b – back extraction ratio [-],
E_f – forward extraction ratio [-],
M_{MC} – mass of microcapsules [g],
$N_{a,1}$ – agitation speed in first emulsification [rpm],
R_f – initial forward extraction rate of Pd(II) [mmol/g·s],

S – specific surface area of microcapsules [m^2/g],
t – time [min],
V_D – pore volume [ml/g],
V_{sol} – volume of aqueous solution [dm^3],
Δt – initial extraction time [sec].

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