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PREPARATION OF EFFECTIVE AND FAST EXTRACTION MEDIA FOR PALLADIUM (II) USING MICROCAPSULES

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ABSTRACT

Microcapsules containing tri-*n*-octylamine as an extractant with the diameter of less than 25μm were prepared by using SPG membrane emulsification and *in-situ* polymerization method. The morphologies of microcapsules, the encapsulation efficiencies of tri-*n*-octylamine, the extraction properties of palladium (II) from hydrochloric acid solution and the back extraction properties of palladium (II) from microcapsules were investigated. The average diameter of obtained microcapsules was about half of the pore diameter of SPG membrane. The encapsulation efficiency of tri-*n*-octylamine was approximately 100% for all the microcapsules prepared in this study. Therefore, it can be said that there was practically no loss of tri-*n*-octylamine during the preparation of microcapsules. All microcapsules prepared in this study reached forward extraction equilibrium within 5 minutes and the forward extraction ratio reached nearly 1. The back extraction of palladium (II) from microcapsules was carried out using 0.1M-hydrochloric acid solution containing a prescribed amount of thiourea. The back extraction occurred promptly and the back extraction ratio was high enough to elute all palladium (II) out from the microcapsules. Furthermore, by repeating forward and back extraction experiments, the durability of microcapsules was examined. From the result, it can be said that tri-*n*-octylamine was encapsulated rigidly and there was no leakage during extraction and back extraction experiment. Thus it seemed that the microcapsules were capable to be used in a repeated operation.

Keywords: Extraction, Microcapsule, Palladium, Tri-*n*-octylamine

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INTRODUCTION

Rare and precious metals such as chromium, vanadium, gold, platinum etc. have special characteristics over base metals and are used in various ways such as semi-conductors, decorative materials, dental materials, industrial catalysts etc. In particular, precious metals are extremely expensive and their supply system is very unstable, because of their limited amount of production, technical difficulties such as they are hard to be purified because of their chemical properties and also political problems of producer countries. Additionally, there have been a rapid progress in high technological industries and a rise of awareness about environmental issues, it is expected that the rare and precious metals demand for semi-conductors and catalytic converters will increase. For the stable supply of these valuable metals, minimization of their waste should be achieved hence it is necessary to establish an effective recovery technique for these metals. Liquid-liquid extraction method has been used in the recovery of metals from aqueous phase [1-3]. This method has several advantages such as high selectivity of diverse metal ions, capableness for treatment of large amount of waste water and easiness to scale-up. However, this method uses a large amount of organic solvent, hence there has been a concern about the influence on the environment and human bodies. Also, the distribution of organic phase into aqueous phase occurs and it complicates the post-treatment of effluents and the regeneration of extractant. Therefore, alternative extraction methods have been studied and proposed by many researchers. For example, extraction method using ion-exchange resin [4], solvent impregnated resin [5,6], supported liquid membrane [7-9] and microcapsules [10-12] can be listed. We have been researching on microcapsules containing tri-*n*-octylamine, hereafter TOA, in extraction of palladium (II) from hydrochloric acid solution [13,14]. From the results of our research so far, it can be said that the microcapsules are effective extraction media for palladium (II). However, the diameter of microcapsules which we have been studying so far was more than 300μm, therefore the diffusion of palladium (II) into microcapsules takes time and it causes the slow extraction rate. Furthermore, in the case of microcapsules with high content of TOA, the highly concentrated palladium (II) complexes near the surface of the microcapsules prevent TOA inside of microcapsules from reacting with palladium (II) and it results in low extraction ratio. To solve these problems, we attempted to reduce the diameter of the microcapsules. It can be expected that the internal diffusion step can be shortened by reducing the microcapsule diameter, and also the amount of TOA, which remains un-reacted inside of microcapsules, can be reduced. In this study, microcapsules containing TOA with a diameter of less than 25μm were prepared using SPG membrane and *in-situ* polymerization method. The morphologies of microcapsules, the encapsulation efficiencies of TOA, the forward extraction and back extraction properties of palladium (II) and also the durability of the microcapsules were investigated.

EXPERIMENTAL

Materials and Apparatus

Divinylbenzene (hereafter DVB) was obtained from Wako Pure Chemicals Industries and washed with 10wt% of sodium hydroxide solution to remove the polymerization inhibitor before it was used. TOA, toluene, 2,2'-azobis(2,4-dimethylvaleronitrile) (hereafter ADVN), gum arabic, hydrochloric acid, ethanol, butanol, thiourea and palladium (II) chloride were also purchased from Wako Pure Chemicals Industries and used without further purification. SPG emulsification apparatus was purchased from SPG Technology Co., LTD.

PROCEDURES

Preparation of microcapsules containing TOA

The organic phase was composed of TOA as the extractant, DVB as the wall material of microcapsules, toluene as the diluent, and ADVN as the initiator. 2wt% of gum arabic solution was used as the outer aqueous phase. The organic phase was poured into the outer aqueous phase and emulsification was carried out using SPG membrane emulsification method for a prescribed time. After emulsification, in-situ polymerization was held by raising the temperature up to 343 K with stirring at 400rpm under nitrogen atmosphere for 5 hours. Then microcapsules containing TOA were obtained by filtration, washing with distilled water and finally drying under vacuum.

Measurement of microcapsule properties

The average diameter of emulsion, D_E and microcapsules D_M were determined from the photographs taken by optical microscopy and scanning electron microscopy respectively. Encapsulation efficiency of TOA (E), and amount of encapsulated TOA per 1g of microcapsules, (E') were measured using the following procedures. First, TOA in the microcapsules was eluted out using a Soxhlet extractor with ethanol. Then the neutralization titration was carried out using 0.1M-HCl solution in the mixture of methanol and butanol to determine the amount of TOA and calculations are as follows;

$$E'_{\max} = \frac{M_{TOA} / Mw_{TOA}}{M_{TOA} + M_{DVB}} \quad \text{[mmol/g]}$$

$$E' = \frac{M'_{TOA} / Mw_{TOA}}{M_{MC}} \quad \text{[mmol/g]}$$

$$E = \frac{E'}{E'_{\max}} \times 100 \quad \text{[\%]}$$

After elution of TOA, the specific surface area (S), and the average pore diameter of microcapsules (D_P), were measured by using a Micromeritics Automatic Surface Area Analyzer (SHIMADZU 2370).

FORWARD EXTRACTION OF PALLADIUM (II) FROM HYDROCHLORIC ACID SOLUTION

As a pretreatment, the microcapsules were put into 2 M-HCl solution and then shaken at 150 rpm at 298K for 24 hours. After filtration and drying under vacuum, microcapsules containing TOA HCl salt were obtained. As the forward extraction experiment of palladium (II), the pretreated microcapsules were dispersed into 0.1M-HCl solution containing a prescribed amount of $PdCl_2$ and then shaken at 150 rpm at 298K for a prescribed time. Then the solution was filtrated and the concentration of residual palladium (II) in the solution was measured using an inductively coupled plasma spectrometer (Nippon JARRELLASH, IRIS Advantage, hereafter called ICP). The extraction equilibrium equations are shown below. The forward extraction ratio (E_f), and the initial forward extraction rate (R_f), were defined as follows:

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

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

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

$$R_f = \frac{C_{Pd_{ext},MC,\Delta t}}{\Delta t} \qquad [\mathrm{mmol/g{\cdot}s}]$$

BACK EXTRACTION OF PALLADIUM (II) FROM MICROCAPSULES

Microcapsules pretreated with HCl were dispersed into 0.1M-HCl solution containing an excess amount of $PdCl_2$ and then shaken at 150 rpm for 24 hours. After filtration and drying under vacuum, microcapsules containing palladium (II) complexes were obtained. Then the microcapsules containing palladium (II) complexes were put into 10mM of thiourea in 0.1M-HCl solution, and back extraction was carried out with shaking at 150 rpm at 298K for a prescribed time. Finally, the concentration of eluted palladium (II) was measured using ICP. The back extraction ratio (E_b), and the initial back extraction rate (R_b), were defined as follows:

$$E_b = \frac{C_{Pd_{elu},sol}\cdot V_{sol}}{C_{Pd,MC,ini}\cdot M_{MC}} \qquad [-]$$

$$R_b = \frac{C_{Pd_{elu},sol,\Delta t}}{\Delta t} \qquad [\mathrm{mmol/l{\cdot}s}]$$

RESULTS AND DISCUSSION

Figure 1 shows the SEM photograph of microcapsules prepared in this study. The prepared microcapsules have a smooth spherical surface. The relations between the pore diameter of SPG membrane and properties of microcapsules are shown in Fig.2.

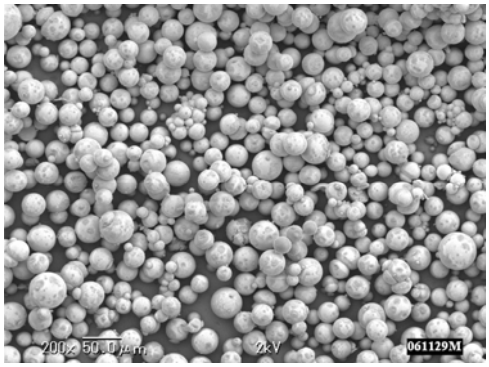

Fig. 1. SEM observation of microcapsules prepared by SPG membrane emulsification method.

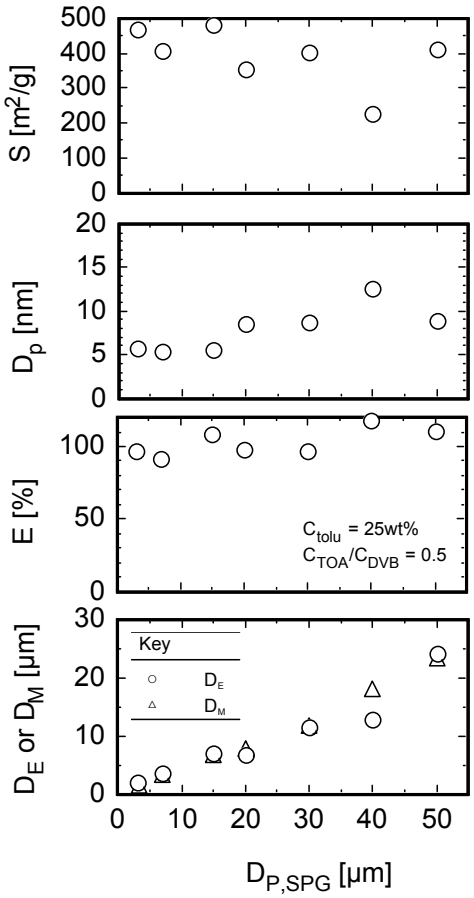

Fig. 2. Effect of SPG pore diameter on the characteristics of microcapsules.

The average diameter of prepared microcapsules was about half of the pore diameter of SPG membrane. From this result, it can be suggested that it is possible to control the size of microcapsules by changing the pore diameter of SPG membrane. The encapsulation efficiencies of TOA were nearly 100% for all the microcapsules prepared in this study. Therefore, it can be said that there is no loss of TOA during the preparation of microcapsules. Figure 3 shows the effect of SPG pore diameter on the pore distribution of microcapsules. From the results shown in Fig.2 and 3, it can be concluded that D_M did not affect D_P, S and the pore distribution of microcapsules. Thus, it seems that the inner structure of microcapsules was not influenced by the size of microcapsules.

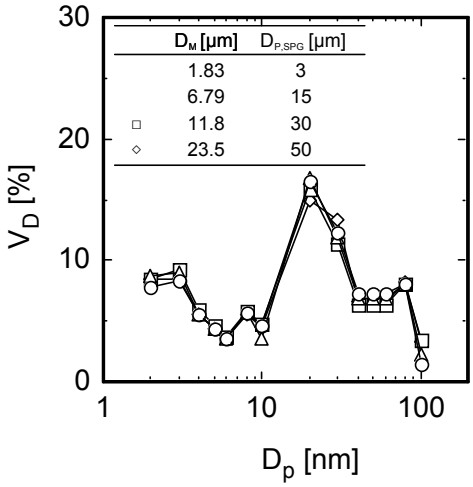

Fig. 3. Effect of SPG pore diameter on the pore distribution of microcapsules.

The results of forward extraction of palladium (II) using microcapsules are shown in Fig.4. As shown in Fig.4, the forward extraction of palladium (II) was occurred promptly, and all microcapsules reached the forward extraction equilibrium within 5 minutes. Besides, the forward extraction ratios were almost 1 for all the microcapsules prepared in this study. Therefore, it can be said that most of encapsulated TOA could react with palladium (II). These results are explained as follows. Because of the reduction of microcapsule diameter, the internal diffusion length of palladium (II) into microcapsules was shortened and it resulted in the less time to reach forward extraction equilibrium. Also, the amount of un-reacted TOA that remains inside of microcapsules was reduced by decrease of diameter of microcapsules and it led to high values of E_f. Also the TOA·HCl salt inside of microcapsules exists as itself, in other words there is no diluent in the microcapsules, so it can be said that the concentration of TOA·HCl salt is extremely high in the microcapsules. Thus, the reaction

rate between TOA·HCl salt and palladium (II) to form complexes is very fast and it contributes to the fast extraction rate. From these results, it can be suggested that it is possible to prepare microcapsules having high extraction ratio and fast extraction rate by using SPG emulsification method.

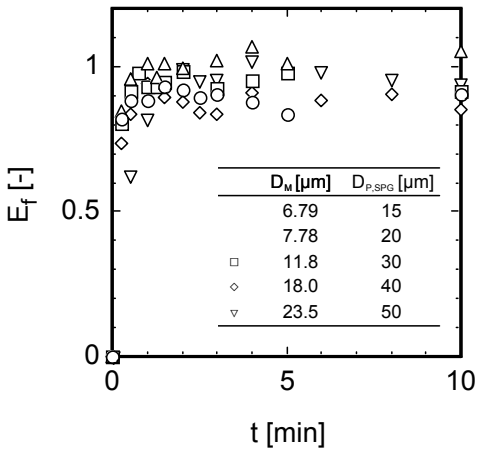

Fig. 4. Effect of SPG pore diameter on the extraction properties of palladium.

The effect of D_M on the initial forward extraction rate of palladium (II) is shown in Fig.5. R_f decreased as D_M was increased. The increase of D_M causes the decrease of the surface area per unit mass of microcapsules. The less surface area means the less TOA·HCl salt exists near the surface of the microcapsules. On the other hand, from the result shown in Fig.2, S was not affected by D_M. The value of S includes the surface area of the pores on microcapsules. According to the results in Fig.2 and 5, it can be assumed that the extraction rate is dependent on only the surface area of microcapsules excluding the pores. Therefore, in the case of microcapsule prepared in this study, it can be said that the diffusion of palladium (II) ions into the pores on microcapsules has little influence on the extraction of palladium (II). The internal diffusion of palladium (II) ions into microcapsules seems to be taking place mainly through the surface of microcapsules. When the values of D_M ares less than 20μm, no correlation was observed between R_f and D_M. This result is considered as follows. Because of reduction of D_M, all of the TOA·HCl salt in the microcapsules could react with palladium (II) instantly. Thus, in the range, R_f was too fast to determine the difference between each size of microcapsules by using the batch-wise experiment.

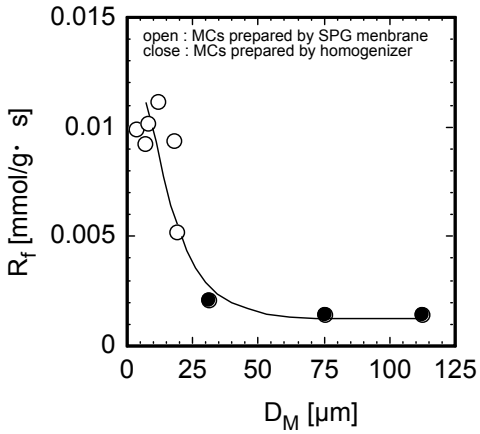

Fig. 5. Effect of microcapsule diameter on the forward extraction rate of palladium.

The effect of toluene concentration on the forward extraction of palladium (II) is shown in Fig.6. Toluene in organic phase evaporates during preparation of microcapsules and creates pores on microcapsules. Therefore, it is expected that the increase of the toluene concentration in organic phase creates more pores on microcapsules. However, the extraction properties were not affected by the concentration of toluene. The relation between R_f and the concentration of toluene is shown in Fig.7. R_f can be considered as constant against the toluene concentration. These results support the result of Fig.5, that is, the diffusion of palladium (II) into pores has little effect on the extraction of palladium (II) in the case of microcapsules prepared in this study.

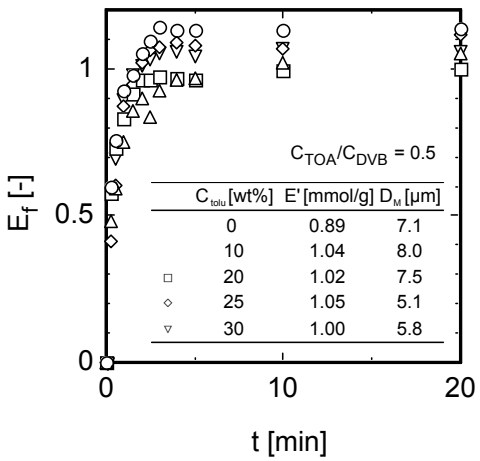

Fig. 6. Effect of toluene concentration on the extraction property of palladium.

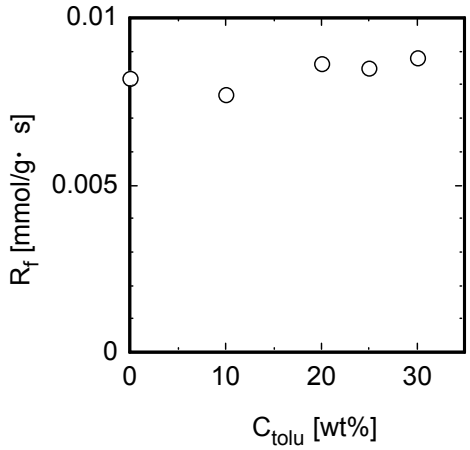

Fig. 7. Effect of toluene concentration on the forward extraction rate of palladium.

Figure 8 shows the effect of TOA concentration in organic phase on the extraction properties of palladium (II). Every sample of microcapsules shows high value of E_f. This is because of the reduction of the microcapsules diameter as well. However, as E' increased, the internal diffusion step, where the extraction ratio increases gradually with time appears. This is caused by that the highly concentrated Pd (II) complexes nearby the surface of the microcapsules obstructed the formation of another Pd (II) complex. But this result only represents how fast the TOA in microcapsules is used up.

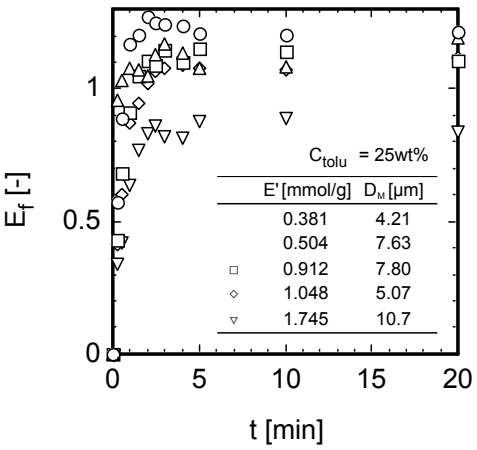

Fig. 8. Effect of TOA concentration on the extraction properties of palladium.

The effect of E' on the initial extraction rate is shown in Fig.9. R_f increased with an increase of E'. From these results, to obtain microcapsules

having swift extraction ability and a high capacity of extraction, *E*' must be controlled properly, as the internal diffusion step would not appear.

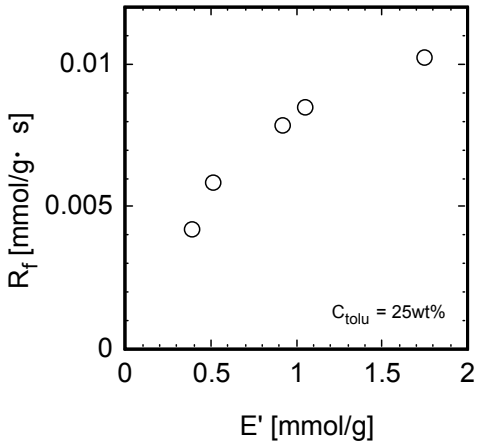

Fig. 9. Effect of TOA concentration on the forward extraction rate of palladium.

The result of the back extraction experiment is shown in Fig.10. E_b reached 1 and the back extraction completed in a short period. Also the back extraction properties were improved by adding HCl. This result is also seen in Fig.11 showing the effect of HCl concentration on the initial back extraction rate. However, slight difference can be observed with increasing the concentration of HCl. Thus, it can be concluded that it is possible to elute all palladium out using a low concentration solution of thiourea in HCl.

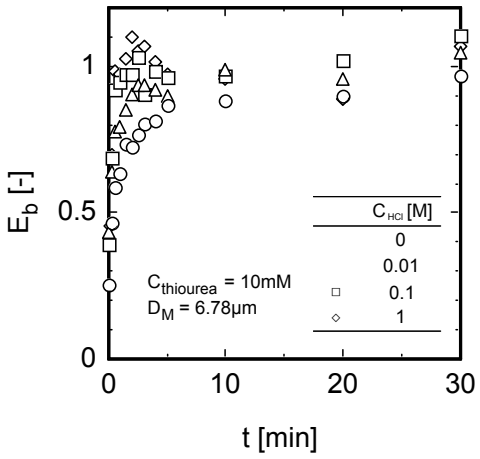

Fig. 10. Effect of HCl concentration of thiourea solution on the back extraction of palladium.

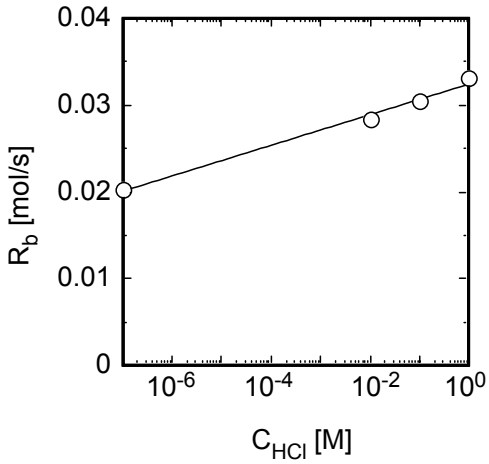

Fig. 11. Effect of HCl concentration on the back extraction rate of palladium.

Lastly, the durability of microcapsules was determined by repeating the extraction and back extraction experiments of palladium (II) and examining whether there is a loss of TOA during experiments or not. The results are shown in Fig.12 As we can see from Fig.12, the microcapsules prepared in this study maintained their high value of E_f and E_b even in the 10 times experiments. Therefore, it can be said that there is no loss of TOA during extraction and back extraction of palladium (II) and the microcapsules are capable to be used in a repeated operation.

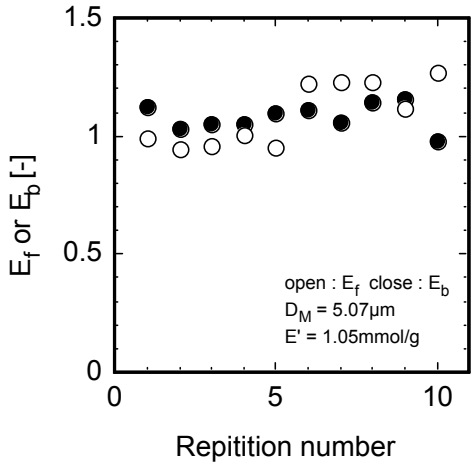

Fig. 12. Durability test of microcapsules.

CONCLUSIONS

Microcapsules containing tri-*n*-octylamine as an extractant with the diameter of less than 25 μm were prepared by using SPG membrane emulsification and *in-situ* polymerization method, and following conclusions were drawn.

1) The microcapsules reached the forward extraction equilibrium within 5 min. The forward extraction ratio was nearly 1 for all microcapsules. The initial forward extraction rate decreased with the increase of the average diameter of microcapsules.
2) To obtain microcapsules having fast extraction rate and high capacity of extraction, it is necessary to control the concentration of tri-*n*-octylamine properly.
3) The back extraction was completed in a short period of time and the back extraction ratio was high.
4) The durability of microcapsules was examined by repeating the extraction and back extraction experiments. The microcapsules kept their high value of extraction ratio even in the 10 times experiments, therefore the microcapsules were capable to be used in a repeated operation.

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.	[mmol/g]
$C_{Pd,ext,MC,\Delta t}$: Pd (II) concentration 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]
$C_{thiourea}$: thiourea concentration in hydrochloric acid solution.	[mmol/dm^3]
C_{TOA} : tri-n-octylamine concentration in organic phase.	[wt%]
C_{tolu} : toluene concentration in organic phase.	[wt%]
D_E : average diameter of emulsion.	[μm]
D_M : average diameter of microcapsules.	[μm]
D_p : average pore diameter of microcapsules.	[nm]
$D_{P,SPG}$: average pore diameter of SPG membrane.	[μm]
E : encapsulation efficiency of TOA.	[-]
E_b : back extraction ratio.	[-]
E_f : forward extraction ratio.	[-]
E'_{max} : maximum amount of encapsulated TOA in microcapsules.	[mmol/g]
E' : amount of encapsulated TOA in microcapsules.	[mmol/g]
M_{DVB} : mass of DVB.	[g]
M_{MC} : mass of microcapsules.	[g]
M_{TOA} : mass of TOA.	[g]
Mw_{TOA} : molecular weight of TOA.	[g/mol]
R_b : initial back extraction rate of palladium (II).	[mmol/l·s]
R_f : initial forward extraction rate of palladium (II).	[mmol/g·s]
S : specific surface area of microcapsules.	[m^2/g]
t : time.	[min]
V_D : pore volume ratio.	[%]
V_{sol} : volume of aqueous solution.	[dm^3]
Δt : initial extraction time.	[sec]

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