Extraction Equilibrium of Precious Metals from Aqueous Acidic Solutions Using Divinylbenzene Homopolymeric Microcapsules Encapsulating Ternary Amine as a Core Material

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ABSTRACT

Divinylbenzene homopolymer microcapsules having porous membranes encapsulating tri-*n*-octylamine as a core material were prepared by *in-situ* polymerization accompanied by the evaporation of toluene. The extraction equilibria of hydrochloric acid and precious metals in an acidic solution using the prepared microcapsules were measured at 303 K. The addition of toluene into the dispersed phase resulted in the microcapsule membrane having a porous structure due to the toluene evaporation during *in-situ* polymerization, which was verified based on the results obtained both from SEM observation of the microcapsules' morphology and in the extraction equilibrium of hydrochloric acid. Using microcapsules prepared with toluene, hydrochloric acid was sufficiently extracted form an aqueous solution. In contrast, microcapsules prepared without toluene scarcely extracted hydrochloric acid. The microcapsules successfully extracted palladium (II) from the acidic media, and this was explained by the reaction between one palladium ion and two molecules of tri-*n*-octylamine in a similar manner of that taking place in the solvent extraction. The back-extraction of palladium (II) from the microcapsules was expressed by the back reaction of the extraction. Gold (III) and platinum (IV) were also successfully extracted using the prepared microcapsules.

INTRODUCTION

Microencapsulation is a unique technique for enclosing active reagents in a porous polymeric membrane, and has been extensively studied in regard to the elongation of the sustained release of core materials (2, 5, 9-12), the protection of the encapsulating active-reagents (3), and the extraction of metal ions and acids (6-8, 11-16).

The processes of separating target chemicals from aqueous media can be roughly divided into two methods: one is solvent extraction in which an organic solution containing extractants is in contact with an aqueous solution containing target chemicals. Solvent extraction has the possibility of being developed into an efficient process by means of enhancing the molecular design and synthesis of extractants. However, solvent extraction still has some problems in that the phase separation of organic and aqueous phases is difficult and that extractants and/or organic solvents are lost by being dissolved into the aqueous phase. The other method is adsorption in which adsorbents, such as activated carbon and chemically modified synthetic resins, are immersed in an aqueous solution containing target chemicals. The separation method using resins such as ion exchange resins and chelating resins is useful for the treatment of dilute solutions and is frequently used for hydrometallurgy, and for the recovery of valuable materials and the removal of harmful substances from aqueous wastewater. These resins are, however, very expensive due to the difficulty of their preparation. Thus, the separation technique using extractants-impregnated microporous resins (17-24) and Levextrel resins (25-27) for diluent solutions have gathered much attention in these fields. The extractant-impregnated macroporous resins have many advantages from the standpoint of preparation and operation. However, the following disadvantages have been recently

pointed out: all molecules of the impregnated extractant are unreacted by the steric hindrance and the selectivity for the target substance decreased due to the inactivation of the extractant (17).

The microcapsules with porous membrane that encapsulate extractants are expected to be adaptable for separation technology because of the high separation property of the extractant encapsulated, which has been clarified in the solvent extraction, and because of the high capacity of the extracted chemicals utilizing their internal core (6-8, 11-16). Previously, we successfully prepared poly (styrene-co-divinylbenzene) copolymeric microcapsules enclosing tri-*n*-octylamine (hereafter abbreviated as TOA) dissolved in *n*-dodecane by *in-situ* polymerization (9, 10, 15). The extraction property of propionic acid using the microcapsules encapsulating TOA is found to be same as that in solvent extraction. The ammonium salt of TOA with hydrochloric acid has been known as useful for the extraction of precious metals (4, 28, 29).

In regard to the practical application of the microcapsule extraction system, a microcapsule membrane that has a higher strength than that of cross-linked polystyrene is preferable. Polydivinylbenzen homopolymeric membranes (hereafter called poly-DVB membranes) are stronger than cross-linked polystyrene membranes because of the former's highly three-dimensional network, though a highly developed network structure might be expected for the reduction of mass transfer rate. However, this reduction is considered to be able to compensate by the formation of macropores into poly-DVB membranes. We have successfully prepared divinylbenzene homopolymeric microcapsules (hereafter called poly-DVB microcapsules) with highly porous membranes enclosing TOA by *in-situ* polymerization accompanied by an evaporation process using volatile solvents (30).

Furthermore, the extraction of hydrochloric acid can be effectively achieved using the microcapsules having macropores. In this paper, microcapsules having highly porous poly-DVB membranes enclosing TOA are prepared by *in-situ* polymerization accompanied by the solvent evaporation, and the extraction characteristics of precious metals from an acidic aqueous solution using the prepared microcapsules are investigated.

EXPERIMENTAL

Reagents

Divinylbenzene (hereafter called DVB) used as a monomer was purchased from Wako Pure Chemicals Co. and purified by a distillation under reduced pressure of nitrogen atmosphere. The distilled DVB was stored in a refrigerator until it was used. 2,2'-Azobis(2,4-dimethylvaleronitrile) (hereafter called ADVN) was purchased from Wako Pure Chemical Co. and used as received. Tri-*n*-octylamine (hereafter called TOA) obtained from Wako Pure Chemical Co. was used as an extractant without further purification. Toluene and gum arabic were used without further purification. Reagent grades of hydrochloric acid, palladium (II) chloride, hydrogen hexachloroplatinate (IV) hexahydrate, and sodium tetrachloroaquarate (III) dihydrate were also purchased from Wako Pure Chemical Co. and used as received.

Preparation of Poly-DVB Microcapsules Encapsulating TOA

Poly-DVB microcapsules were prepared by *in-situ* polymerization using ADVN as a polymerization initiator. The experimental apparatus for the preparation of the microcapsules is shown in **Fig. 1**. The reactor was a separated cylindrical flask with a round bottom and was equipped with four baffles of 1/10 the width of the

reactor diameter, and with a two-bladed screw type agitator, a thermometer, and a reflux condenser.

Preparation conditions of poly-DVB microcapsules are listed in **Table 1**. An organic dispersed phase consisted of DVB, TOA, ADVN and toluene as a diluent. An aqueous continuous phase was composed of distilled water containing 2.0 wt% of gum arabic. The continuous phase was put into the reactor and then the organic phase was poured to the continuous phase. The solution was stirred at 6.67 s^{-1} to form O/W emulsion. The reactor was then maintained at 343 K for 28.8 ks. under a nitrogen atmosphere in order to prepare the poly-DVB microcapsules by *in-situ* polymerization. The prepared microcapsules were collected by filtration, washed with water, and finally dried under a vacuum. The residual toluene in the core solution after polymerization was detected to be only 0.1 wt% of the initial toluene. This means that the core solution was pure TOA.

The yield of the microcapsules prepared at various conditions was determined gravimetrically for each experiment. The diameters of the microcapsules were measured microphotographically using a digitizer (MODEL K-510mk2, Logitec Co., Ltd.). More than 300 particles for each run were measured in order to determine the microcapsules' average diameter. SEM observation was carried out using a Hitachi H7010A scanning electron microscope at an intensity of 10 kV under various magnifications; great care was used to minimize the damage to the microcapsules due to the electron beam.

Extraction Characteristics of Poly-DVB Microcapsules

A prescribed amount of the microcapsules was immersed in an aqueous hydrochloric acid solution, and the solution was shaken in a thermostatic bath at 303 K. After attaining equilibrium, the microcapsules were filtrated and the equilibrium concentration of hydrochloric acid in the filtrate was determined by neutralization titration with 0.1 mol· dm^{-3} NaOH aqueous solution using phenolphthalein as an indicator. The results of the preliminary experiment determined that several hours are enough to attain the extraction equilibrium for the microcapsules prepared with toluene; however, for the microcapsules prepared without toluene, the extraction equilibrium was not reached for several hours. Therefore, the results for the microcapsules prepared without toluene were expressed after immersion at 172.8×10^3 s. The amount of the microcapsules in the aqueous solution was kept at 80 g· dm^{-3}, and the initial concentrations of hydrochloric acid in the aqueous solution were varied from 1.0×10^{-3} mol·dm^{-3} to 3.0 mol· dm^{-3}.

For the measurements of the extraction equilibrium of precious metals with microcapsules, the microcapsules were pretreated with aqueous hydrochloric solution except for the experiment without pretreatment. This treatment caused all molecules of TOA in the microcapsules to react with hydrochloric acid to form its ammonium salt. The pretreated microcapsules were immersed in the aqueous acidic solution containing a precious metal. The amount of the microcapsules added to the aqueous solution was 40 g· dm^{-3}. The concentration of precious metals in the aqueous solution was determined by means of an atomic adsorption spectrometer (AA-625, Shimadzu Ltd.). The concentration of the metals extracted into the microcapsules was estimated based on the mass balance of the metals in the aqueous solution before and after the extraction.

Back-extraction of Palladium from Poly-DVB Microcapsules

Prior to the back-extraction experiment, the microcapsules were immersed in 0.2 mol·dm^{-3} aqueous hydrochloric solution in which was dissolved 5.0 mmol·dm^{-3} $PdCl_2$. The microcapsules extracting palladium (II) were then immersed in new aqueous solutions at various hydrochloric acid concentrations and equilibrated in a thermostatic bath at 303 K. The amount of the microcapsules in the aqueous solution was 40 g·dm^{-3}. The distribution coefficient in the back extraction experiment, D, was calculated based on the difference between the initial palladium (II) concentration contained in the microcapsule and the equilibrium concentration in the aqueous solution after back-extraction.

RESULTS AND DISCUSSION

Preparation and Characteristics of Poly-DVB Microcapsules by *In-situ* Polymerization Accompanied by Toluene Evaporation

The yield and average diameter of the microcapsules prepared are listed in Table 1. A following modified yield, α', which is based on the assumption of toluene during the *in-situ* polymerization process previously reported (30), was also used in this work.

$$\alpha' = W_{MC} / (W_{DVB,0} + W_{B,0}) \qquad \text{Eq.(1)}$$

The values of α' were very high in all preparation conditions. This means that 1) almost all molecules of the DVB monomer used form the microcapsule membranes, 2) TOA which was dissolved in the organic phase was perfectly enclosed in the microcapsules, and 3) almost all of the microcapsules prepared were recovered. Furthermore, it was confirmed by gas chromatographic measurements that toluene did not remain in the core solution and was less than 0.1 wt%.

A microphotograph of the microcapsules prepared with toluene, MC-2, is shown in **Fig. 2**. The microcapsules were spherical in shape and had a relatively large distribution of diameters. The same spherical microcapsules were obtained under all the preparation conditions examined. The average diameter of the microcapsules was affected by the extent of toluene in the organic phase. The average diameter of the microcapsules prepared with small amounts of toluene, MC-3 and MC-4, tend to be almost same as that without toluene and tend to be larger than that of higher toluene contents, MC-2 and MC-3. This difference of the average diameter may reflect the difference of the formation process of O/W emulsion by the difference of viscosity in the organic phase and/or the membrane structure of the microcapsules due to the difference of the amount of evaporated toluene during the preparation.

In order to clarify the membrane structure and morphology of the microcapsules, the surface and cross section of the microcapsules, which would reflect toluene evaporation, were observed via SEM. The surface morphologies of the microcapsules prepared with toluene, MC-2, and without toluene, MC-1, are shown in **Fig. 3**. The surface of MC-1 prepared without toluene was smooth and uniform, and no holes such as pores were observed on the surface. On the other hand, many pores of a few μm in diameter were observed on the surface of MC-2 prepared with toluene. The same surface morphologies were observed for the other microcapsules prepared with toluene. **Figure 4** shows SEM photographs of the cross sections of the microcapsules as shown in Fig. 3. The membrane of MC-1 was a uniform and dense structure, a porous structure not being observed. The membrane of MC-2, however, had a highly porous structure, formed with microcapsules

prepared in this work which were found to be mono-cored. The formation of pores in a polymeric membrane was recognized in microcapsules produced using toluene.

Extraction of Hydrochloric Acid with Poly-DVB Microcapsules

Prior to the experiment regarding the extraction of precious metals, the extraction equilibrium of hydrochloric acid was measured using the prepared microcapsules. TOA is a typical extractant for various acids and its extraction equilibrium has been clarified (1,4). The ammonium salt of TOA, which is formed by the reaction between TOA and hydrochloric acid, is a useful extractant for precious metals (28, 29).

The extraction of hydrochloric acid with TOA is presented by following reaction:

$$B + HCl = B \cdot HCl \qquad \text{Eq. (2)}$$

Kawano *et al*. introduced the apparent association number, *Z*, to estimate the extraction equilibrium constant (1). *Z* is defied as the number of hydrochloric acid molecules extracted by one molecule of TOA and is given by the following equation:

$$Z = (C_{HCl,aq,0} - C_{HCl,aq}) \cdot V / (C_{B,MC,0} \cdot W), \qquad \text{Eq. (3)}$$

where $C_{HCl,aq}$ is the acid concentration in the aqueous solution, V is the volume of the aqueous solution, W is the weight of the microcapsules added to the solution, and $C_{B,MC}$ is the TOA concentration in the microcapsules.

The results of hydrochloric acid extraction using the microcapsules prepared with and without toluene, MC-2 and MC-1, respectively are shown in **Fig. 5**. The values of *Z* are plotted against the equilibrium concentration of the acid. In the case of MC-1, the values of *Z* were very low even in the high concentration range of hydrochloric acid. Since there are no macropores in the surface and the membrane of

MC-1 as suggested from Figs. 3-(a) and 4-(a), it is considered that the mass transfer in the extraction is prevented or that additional time is needed for effective extraction. In contract, the values of *Z* for MC-2 prepared with toluene increased with increasing concentrations of hydrochloric acid in the aqueous solution and approached 1.0 at a high hydrochloric acid concentration. This clearly shows that TOA in the microcapsules reacts with one molecule of hydrochloric acid to form a 1:1 complex and that the extraction property expresses a manner to that in the solvent extraction. This result indicates that macropores made by toluene evaporation during polymerization work are effective as channels for the extraction of hydrochloric acid as suggested from Figs. 3-(b) and 4-(b). The effect of initial toluene content on the extraction properties of the microcapsules prepared with toluene was not observed under the condition examined.

Extraction Equilibrium of Palladium (II) from Aqueous Acidic Solution with Poly-DVB Microcapsules

The complexation of palladium (II) with chloride ions in an aqueous chloride media is given by the following equation:

$$Pd^{2+} + iCl^{-} = PdCl_i^{(i-2)-} \quad (i=1–4). \qquad \text{Eq. (4)}$$

From the distribution calculation of palladium chloro-complexes (28, 31), the majority of palladium (II) exists as a tetrachloride complex, $PdCl_4^{2-}$, in the concentration region of chloride ions used in the present study, while concentrations of the other species of palladium (II) which are Pd^{2+}, $PdCl(H_2O)_3^{+}$, $PdCl_2(H_2O)_2$ and $PdCl_3(H_2O)^{-}$ are negligible compared with that of tetrachloride complex, $PdCl_4^{2-}$.

In the solvent extraction of palladium (II) using TOA ammonium salts from the aqueous solution, $PdCl_4^{2-}$ is extracted into the organic phase, and the extraction reaction is expressed as follows (28):

$$2BHCl + PdCl_4^{2-} = (BH)_2PdCl_4 + 2Cl^- . \quad \text{Eq. (5)}$$

Therefore, the equilibrium constant, K_{Pd}, for the above equation can be expressed as follows:

$$K_{Pd} = \{(C_{(BH)_2PdCl_4,MC})\cdot(C_{C1,aq})^2\}/\{(C_{BHCl,MC})^2\cdot(C_{PdCl_4^{2-},aq})\}$$
$$= \{D_{Pd}\cdot(C_{Cl,aq})^2\}/(C_{BHCl,MC})^2 , \quad \text{Eq. (6)}$$

where, D, the distribution ratio for palladium (II) is defined as the following relation:

$$D_{Pd} = C_{Pd,MC} / C_{Pd,aq}$$
$$= (C_{Pd,aq,0} - C_{Pd,aq})\cdot(V/W) / C_{Pd,aq} . \quad \text{Eq. (7)}$$

Equation (6) can be rewritten as follows:

$$D_{Pd} = K_{Pd} \{C_{BHCl,MC} / C_{Cl,aq} \}^2 . \quad \text{Eq. (8)}$$

In this equation, the concentration of free ammonium chloride salt in the core solution encapsulated in the microcapsules was calculated from the mass balance of the chemical species related to the extraction reaction.

In order to elucidate the effects of chloride or hydrogen ions on the extraction equilibrium, the concentrations of both ions were changed by the addition of hydrochloric acid or lithium chloride into 0.2 mol·dm^{-3} aqueous hydrochloric acid solution. The values of the distribution ratio of palladium (II) are plotted against the chloride ion concentration in **Fig. 6.** The distribution ratio of palladium (II), D_{Pd}, decreased linearly with an increase in the concentration of chloride ion and plotted on the same line. No difference between the cases of lithium chloride and hydrochloric acid, which were used to change the concentration of chloride ion, was

observed. It is concluded that the values of D_{Pd} depended only on the concentration of chloride ion as has been determined in solvent extraction (28).

The effects of the initial concentrations of palladium (II) in the aqueous phase and TOA in the microcapsules are shown in **Figs. 7** and **8**, respectively. The distribution ratio of palladium (II), *D*, was plotted against the concentration of chloride ion. *D* decreased with an increase in the concentrations of chloride ion and palladium (II) in the aqueous solution and increased with an increase in the concentrations of TOA in the microcapsules.

All experimental data shown in Figs. 7 and 8 were analyzed based on the extraction reaction of Eq. (5). Based on Eq. (8), the values of *D* were plotted against $C_{BHCl,MC}/C_{Cl,aq}$ on the logarithmic scale shown in **Fig. 9**. All experimental data except for the data at very high values *D* values were plotted on a single straight line having a slope of 2.0. This result shows that the extraction of palladium (II) with TOA enclosing in the microcapsules is also expressed by the reaction of Eq. (5). The intercept of the straight line shown in Fig. 9 gives the equilibrium constant, K_{Pd}, which was determined to be 1.2×10^4 $dm^3 \cdot kg\text{-}MC^{-1}$. The calculated results using K_{Pd} are presented as the solid lines in Figs 7 and 8. The calculations agreed closely with the experimental results.

Poly-DVB microcapsules pretreated with aqueous hydrochloric acid to form TOA ammonium salts were used in the measurement of the extraction equilibrium of palladium (II) described above. Considering the industrial application of microcapsules encapsulating TOA, it is preferable to exclude the pretreatment process. Therefore, the extraction of palladium (II) using the microcapsules without pretreatment with hydrochloric acid was carried out at various initial TOA concentrations. No difference between the results without and with pretreatment was

observed when the hydrochloric acid concentration in the aqueous solution was 1.1 $mol \cdot dm^{-3}$ in which all of TOA molecules are changed to its ammonium salt. This indicates that a TOA molecule was first protonated by hydrochloric acid, after which the reaction expressed by Eq. (6) proceeded in a substantial manner.

Back Extraction Equilibrium of Palladium (II) from Poly-DVB Microcapsules

The back extraction of palladium (II) using aqueous hydrochloric acid solution can be expressed as a back reaction of Eq. (6). Therefore, the equilibrium constant in the back extraction is derived as follows:

$$K'_{Pd} = \{(C_{BHCl,MC})^2 \cdot (C_{PdCl_4^{2-},aq})\} / \{(C_{(BH)_2PdCl_4,MC}) \cdot (C_{Cl,aq})^2\}$$
$$= (C_{BHCl,MC})^2 / \{D' \cdot (C_{Cl,aq})^2\} , \qquad \text{Eq. (9)}$$

where D'_{Pd} is the distribution ratio for palladium (II) in the back extraction which is given by Eq. (9),

$$D'_{Pd} = C_{Pd,MC} / C_{Pd,aq}$$
$$= \{ C_{Pd,MC,0} - (C_{Pd,aq} \cdot V)/W \} / C_{Pd,aq} , \qquad \text{Eq. (10)}$$

Equation (9) can be rewritten as follows:

$$D'_{Pd} = (C_{BHCl,MC} / C_{Cl,aq})^2 / K'_{Pd} . \qquad \text{Eq. (11)}$$

Palladium (II) extracted into the microcapsules at various initial concentrations of TOA was back-extracted using various concentrations of hydrochloric acid. The results of the back extraction of palladium (II) are shown in **Fig. 10**. The values of D'_{Pd} were plotted against the concentrations of chloride ion in the aqueous phase used for the back-extraction. The distribution ratio decreased with an increase in the concentration of chloride ion in the aqueous solution in a manner to that described regarding the extraction of palladium (II).

The experimental results in the back-extraction were analyzed based on Eq. (11). The values of D'_{Pd} were plotted against $C_{BHCl,MC}/C_{Cl,aq}$ on the logarithmic scale in **Fig. 11**. All experimental data were plotted on a single straight line having a slope of 2.0. This result shows that the back-extraction of palladium (II) extracted into the inside of the microcapsules is expressed by the back-reaction of Eq. (5). The intercept of the straight line shown in Fig. 11 gives the reciprocal value of K'_{Pd}. The value of K'_{Pd} was determined to be 2.0×10^{-4} kg-MC·dm^{-3}. This value of K'_{Pd}, which is correspondent to the reciprocal of K_{Pd}, is smaller than the value anticipated from the value of K_{Pd}. This small of K'_{Pd} value suggests that back-extraction occurs only with difficulty in this system. This difficulty concerning back-extraction may be due to slow diffusion velocity in the core solution or the formation of another stable complexes in the core solution. This difficulty in back-extraction using hydrochloric acid will be improved by the use of the appropriate eluent compounds. The calculated results using K'_{Pd} are presented as the solid lines in Fig 10. The calculations agreed closely with the experimental results.

Extraction of Gold (III) and Platinum (IV) from Aqueous Acidic Solution with Poly-DVB Microcapsules

The extraction of gold (III) and platinum (IV) from acidic chloride media using the microcapsules was also carried out at various concentrations of metals and 1.0 mol·dm^{-3} of chloride ion. The extracted fraction, E_M, was defined as follows:

$$E_M = \quad 100\ (C_{M,aq,0} - C_{M,aq})/C_{M,aq,0} \qquad \text{Eq. (12)}$$

The results are shown in **Fig. 12**. In both metals, E_M values were very high under the examined condition. This shows that the prepared microcapsules containing TOA are

also effective for the extraction of gold (III) and platinum (IV). These extraction reactions would be expressed by following reactions:

$$AuCl_4^- + BHCl = BHAuCl_4 + Cl^- \quad \text{Eq. (13)}$$

$$PtCl_6^{2-} + 2BHCl = (BH)_2PtCl_6 + 2Cl^- \quad \text{Eq. (14)}$$

However, further investigations will be required in order to clarify the extraction mechanisms and equilibrium of gold (III) and platinum (IV). The difference of the distribution ratios between these precious metals is relatively small. Thus, the separation of precious metals using the microcapsules prepared in this study is expected to be difficult due to this small difference in distribution ratio. Therefore, we consider that vigorous studies will be performed in the future, postulating the operation of column type equipment and the separation using the elusion process using the microcapsules prepared in this work.

CONCLUSION

Studies of the preparation of divinylbenzene homopolymeric microcapsules enclosing tri-*n*-octylamine as a core material were performed, together with an examination of the extraction equilibria of hydrochloric acid and precious metals from aqueous acidic media. Morphological and extraction properties were investigated by varying the relevant parameters to arrive at the following results. (1) Spherical poly-DVB microcapsules having an average diameter of 170 μm were prepared with and without the addition of toluene into the dispersed phase. Microcapsules with porous membranes can be prepared with the addition of toluene. The *in-situ* polymerization accompanied by solvent evaporation proposed in this work offers a new process for preparing microcapsules with highly porous membranes.

(2) The results of the extraction of hydrochloric acid demonstrated that the pores created by toluene evaporation act as channels for extraction. The effect of preparation conditions such as the concentrations monomer and solvent was not observed.

(3) The extraction mechanism of palladium (II) from the aqueous media using the microcapsules was the same as that in the solvent extraction.

(4) The back-extraction of palladium (II) from the core solution encapsulated in the microcapsules was successfully carried out using aqueous hydrochloric acid solutions. The distribution coefficient of palladium (II) in the back extraction decreased with increases in the concentration of hydrochloric acid in the aqueous solution.

(5) Gold (III) and platinum (IV) were successfully extracted using the prepared microcapsules.

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Figure Captions

Fig. 1 Schematic illustration of reaction vessel used.

Fig. 2 Microphotograph of poly-DVB microcapsules prepared with toluene, MC-2

Fig. 3 SEM photographs of the surface of the microcapsules
a) without the addition of toluene, MC-1, and b) with toluene, MC-2

Fig. 4 SEM photographs of the cross section of the microcapsules
a) without the addition of toluene, MC-1, and b) with toluene, MC-2

Fig. 5 Extraction property of hydrochloric acid using the microcapsules prepared without of toluene, MC-1, and with toluene, MC-2.

Fig. 6 Effect of the chloride ion concentration on the distribution ratio of palladium(II), D_{Pd}, using the microcapsules prepared with toluene, MC-2.

Fig. 7 Effect of the chloride ion concentration on the distribution ratio of palladium(II), D_{Pd}, at various initial palladium concentrations in the aqueous phase using the microcapsules prepared with toluene, MC-2.

Fig. 8 Effect of the chloride ion concentration on the distribution ratio of palladium(II), D_{Pd}, at various initial TOA concentrations in the microcapsules.

Fig. 9 Plot of the distribution ratio, D_{Pd}, against $C_{BHCl,MC}/C_{Cl,aq}$.

Fig. 10 Effect of the hydrogen ion concentration on the distribution ratio of palladium back-extraction, D'_{Pd}, at various initial TOA concentrations in the microcapsules

Fig. 11 Plot of the distribution ratio in back-extraction, D'_{Pd}, against $C_{BHCl,MC}/C_{Cl,aq}$.

Fig. 12 Extracted fraction of gold(III) and platinum(IV) using the microcapsules prepared with toluene, MC-2

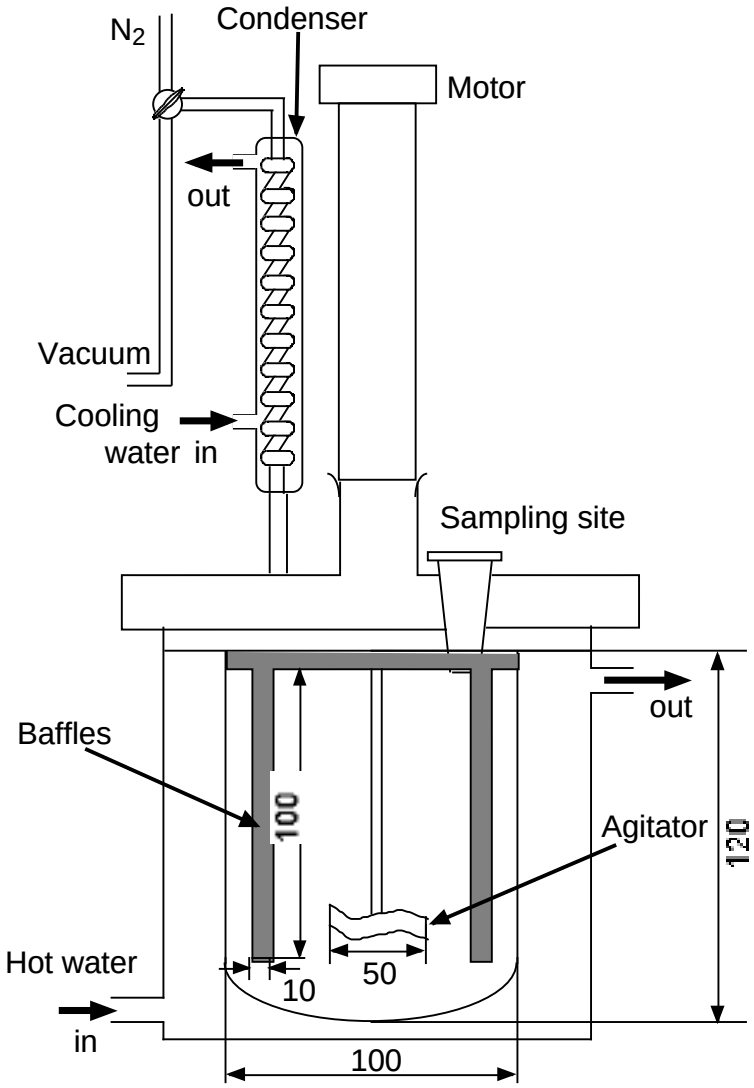

Fig. 1 Schemitic illustration of reaction vessel used.

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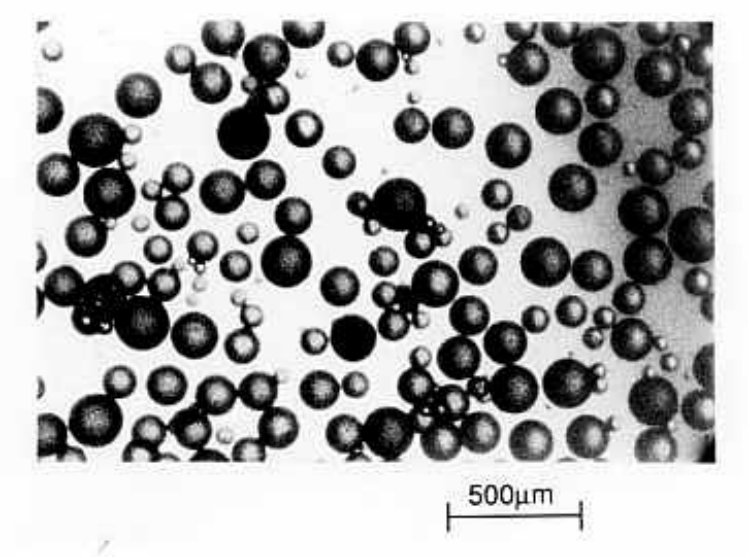

Fig. 2 Microphotograph of poly-DVB microcapsules prepared with toluene, MC-2

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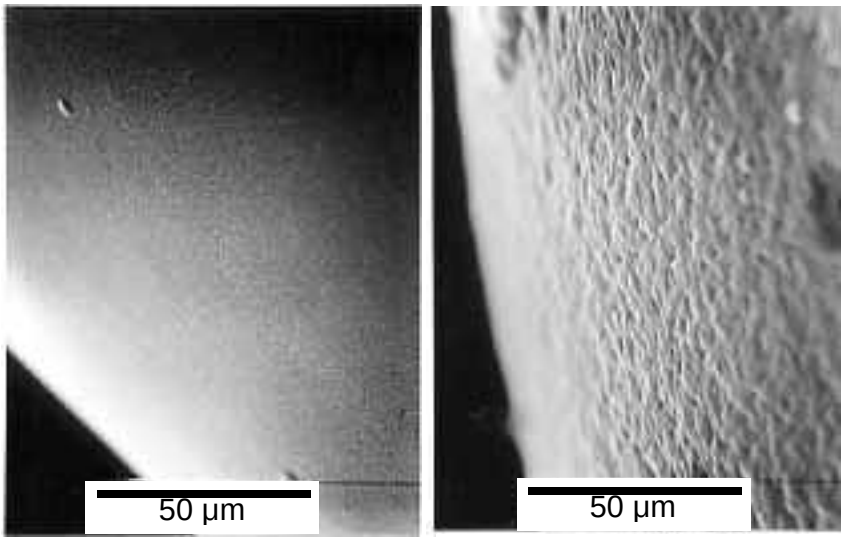
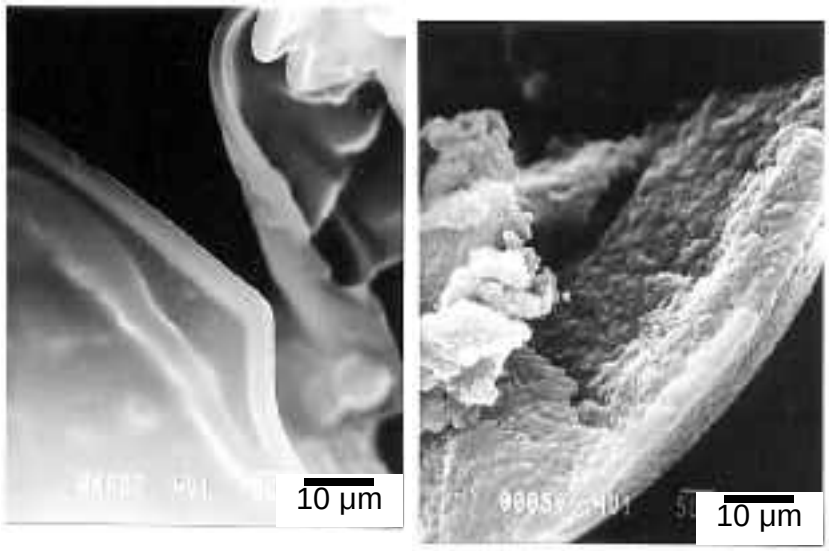


a) MC-1 **b) MC-2**

Fig. 3 SEM photographs of the surface of the micerocapsules
a) without the addition of tolunen, MC-1, and b) with toluene, MC-2



c) MC-1 **d) MC-2**

Fig. 4 SEM photographs of the cross section of the micerocapsules
a) without the addition of tolunen, MC-1, and b) with toluene, MC-2

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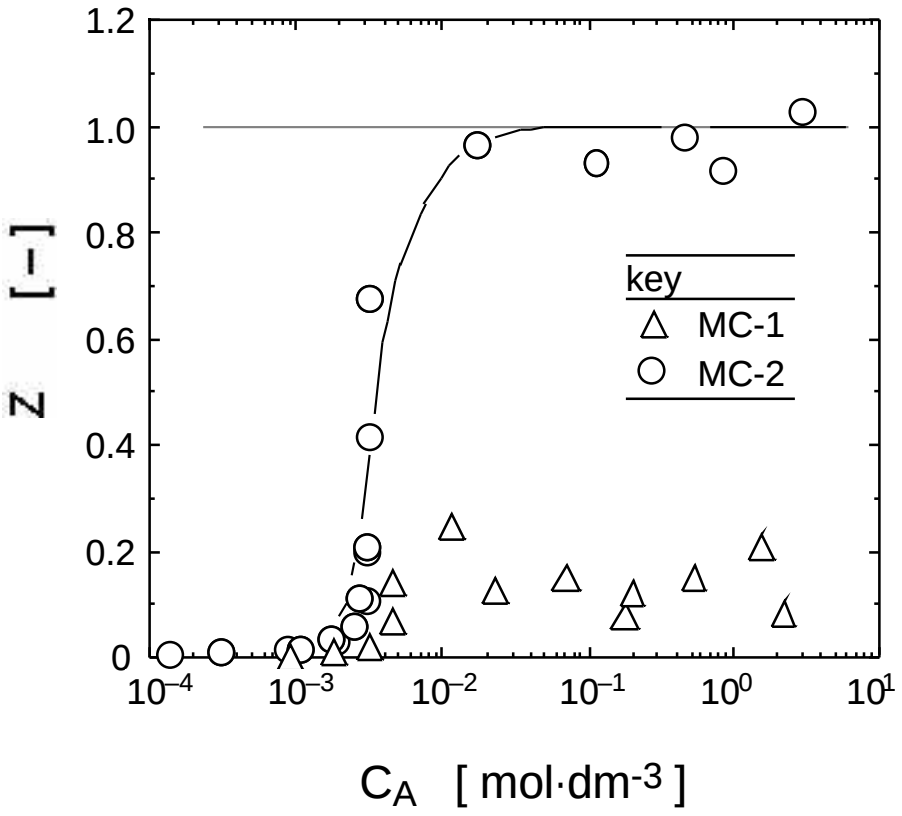


Fig. 5 Extraction property of hydrochloric acid using the microcapsules prepared without of toluene, MC-1, and with toluene, MC-2.

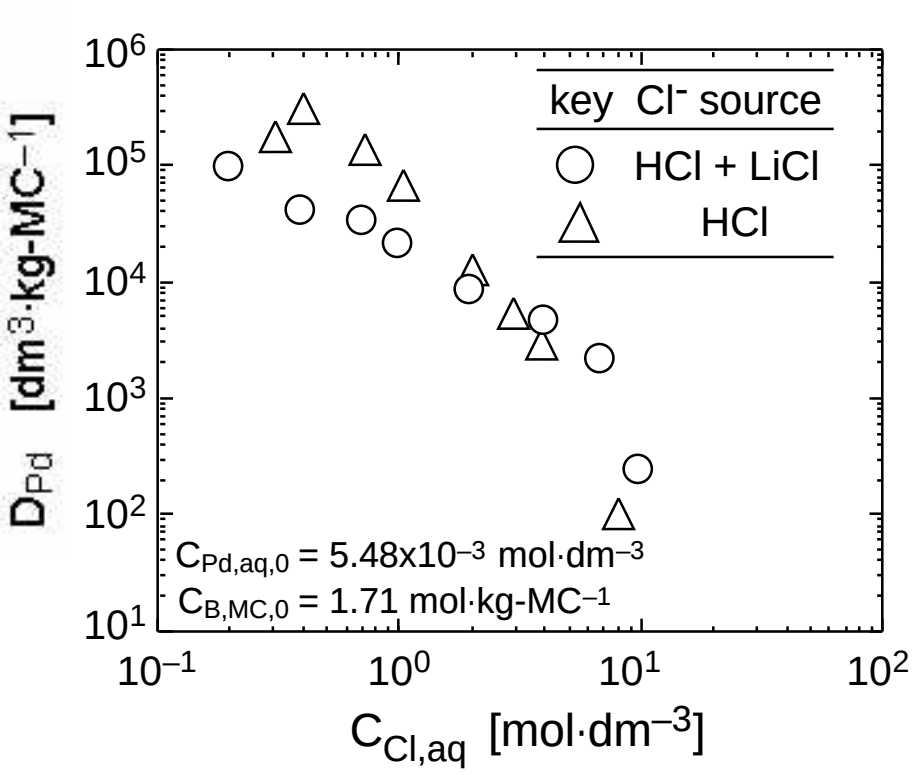


Fig. 6 Effect of the chloride ion concentration on the distribution ratio of palladium(II), D_{Pd}, using the microcapsules prepared with toluene, MC-2.

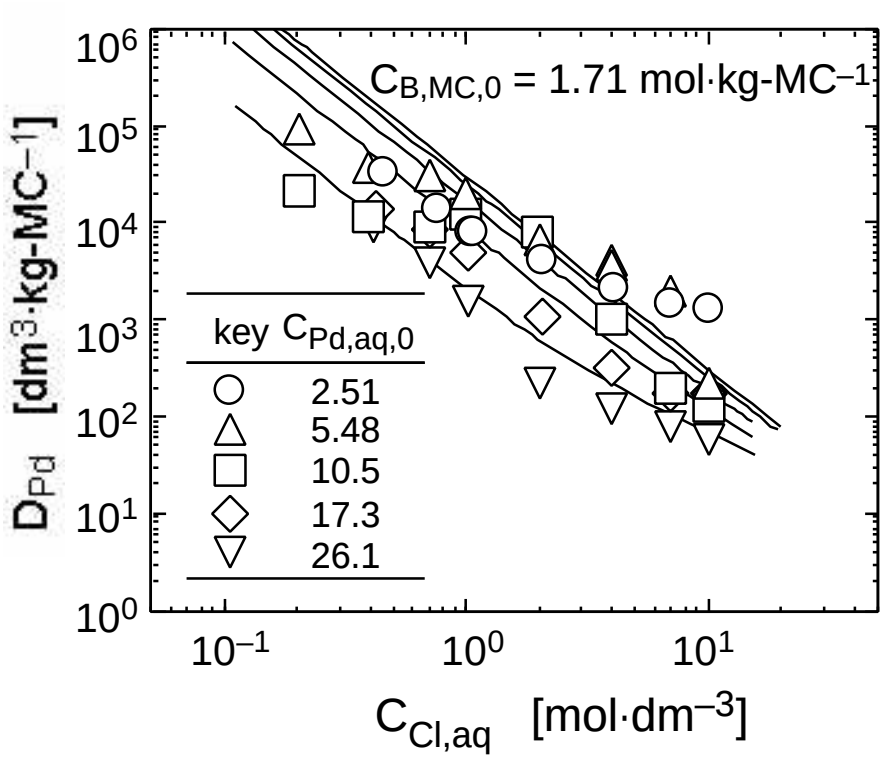


Fig. 7 Effect of the chloride ion concentration on the distribution ratio of palladium(II), D_{Pd}, at various initial palladium concentrations in the aqueous phase using the microcapsules prepared with toluene, MC-2.

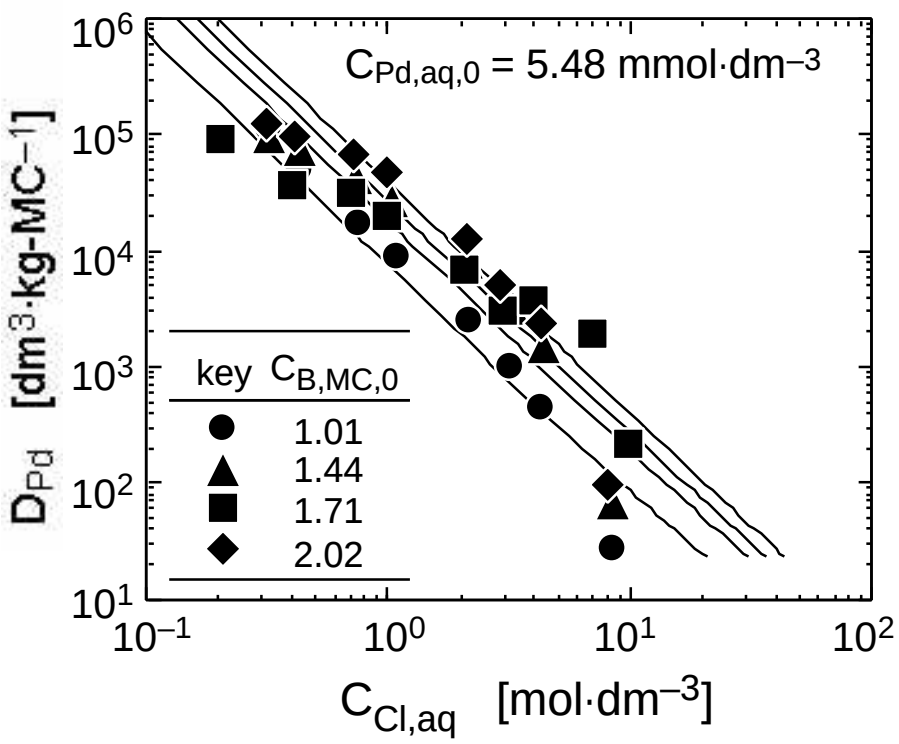


Fig. 8 Effect of the chloride ion concentration on the distribution ratio of palladium(II), D_{Pd}, at various initial TOA concentrations in the microcapsules.

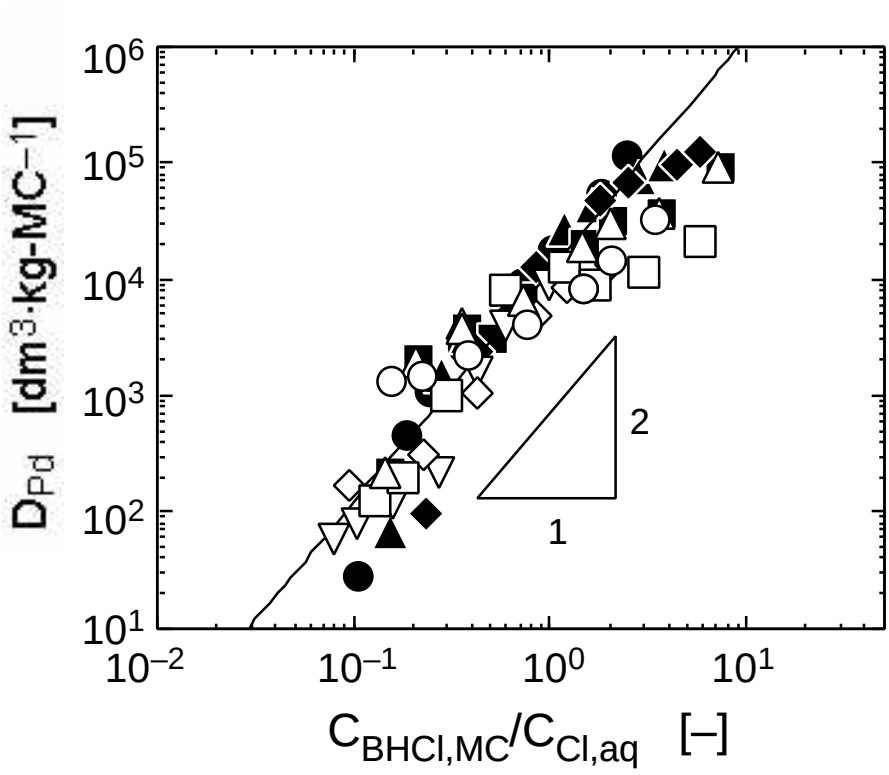


Fig. 9 Plot of the distribution ratio, D_{Pd}, against $C_{BHCl,MC}/C_{Cl,aq}$

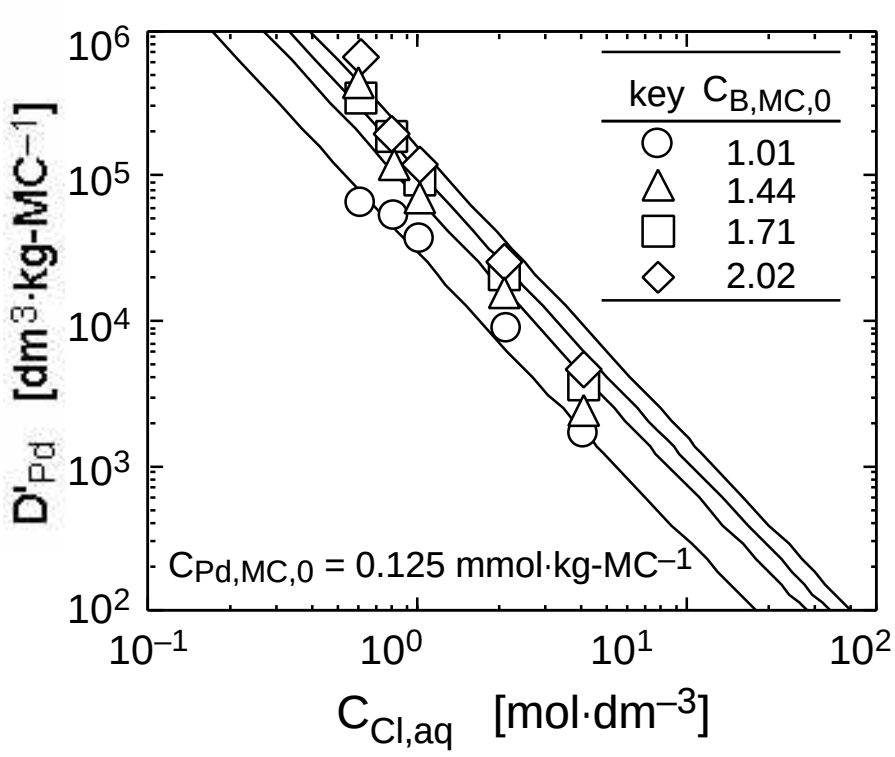


Fig. 10 Effect of the hydrogen ion concentration on the distribution ratio of palladium back-extraction, D'_{Pd}, at various initial TOA concentrations in the microcapsules

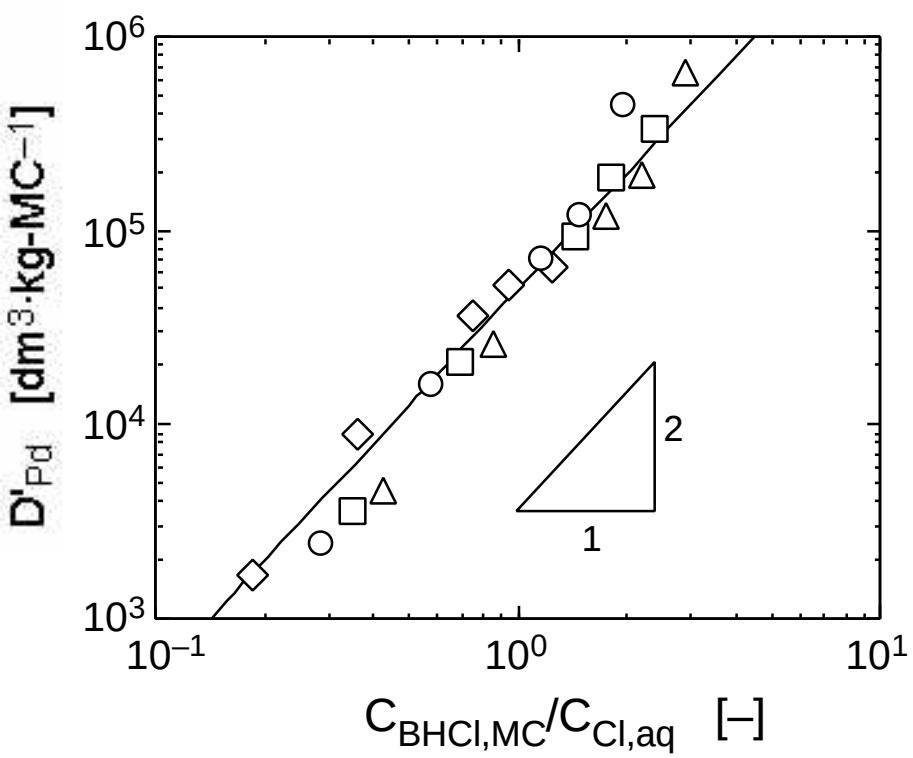
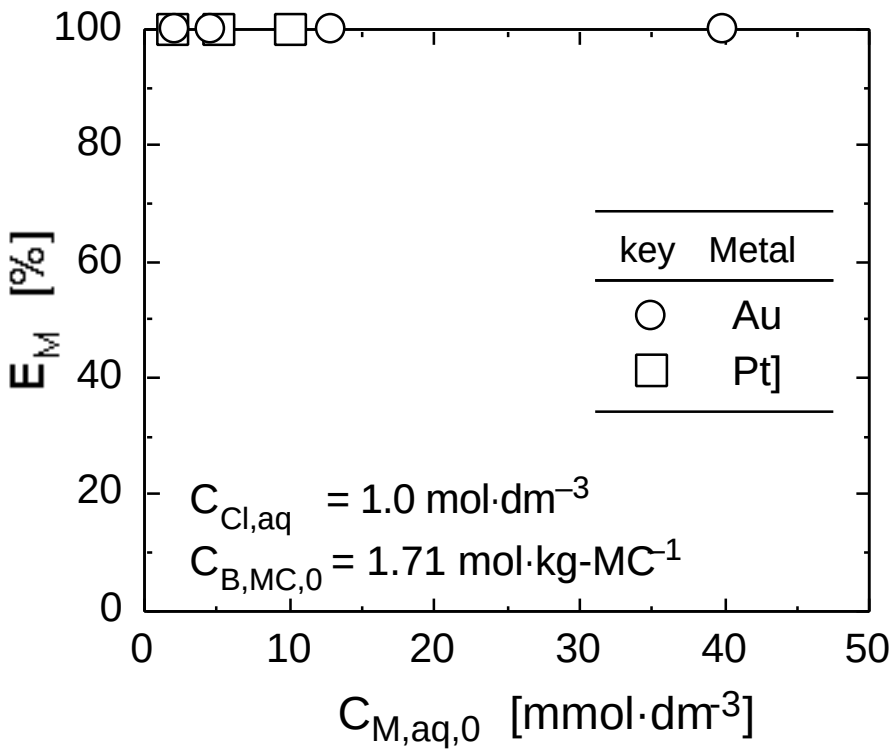


Fig. 11 Plot of the distribution ratio in back-extraction, D'_{Pd}, against $C_{BHCl,MC}/C_{Cl,aq}$.



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