Evaluation of the Interactions Between Palladium(II) and N,N'-Dimethyl-N,N'-di-n-hexyl-thiodiglycolamide in the Presence of Surfactants Using Capillary Electrophoresis

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Abstract
Continuous counter-current foam separation (CCFS) is a method for the recovery of valuable metals with high selectivity. It was developed as an organic solvent-free method, and the interaction of surfactants and metal ions in aqueous solution is a key precondition for the successful recovery. In this study, the interactions between the anionic complex of palladium(II) chloride and N,N'-dimethyl-N,N'-di-n-hexyl-thiodiglycolamide (MHTDA), which is an extraction agent for palladium(II), were investigated by capillary electrophoresis, in the presence of surfactants (sodium dodecyl sulfate (SDS) or polyoxyethylene mono-4-octylphenyl ether (POOPE)). The addition of MHTDA to an electrophoretic media containing SDS, resulted in electropherograms composed of two or three peaks. On the other hand, in the case of an electrophoretic media containing POOPE, the elimination of palladium (II) peak was observed due to MHTDA addition. This behavior suggested that the palladium-MHTDA neutral complex is rapidly captured in the POOPE micelles compared with the SDS micelles, and the use of POOPE is effective for the successful recovery of palladium(II) in CCFS.

Keywords: Palladium; Recovery; Continuous counter-current foam separation; Surfactant

1. Introduction
Recently, the demand for the recovery of valuable metals from waste, to build a 3R (reduce, reuse, and recycle)-oriented sustainable society, has increased. One of the common methods for metal recovery is solvent extraction from an acidic leaching solution of waste [1,2]. However, the use of large amounts of organic solvents in a solvent extraction process generally results in both high cost and high environmental loads. Therefore, an organic solvent-free method for selective metal recovery is imperative, and its deployment is demanded.

Continuous counter-current foam separation (CCFS), developed as an organic solvent-free method, is a method for the recovery of valuable metals with high selectivity [3-6]. In CCFS, a valuable metal (target metal) is separated from coexisting metals (non-target metals), based on the differences in the interactions between the metals and the surfactants layer on the foams. The metal captured on the foam (or surfactants on the foam) with a strong interaction is located in an up-current stream of the foam, while others are in the down-current liquid stream between the foam, which is produced by the addition of a washing solution.
Therefore, the interactions between the surfactants and metal ions are a precondition for successful recovery using CCFS.

In our previous work, we evaluated the interactions between metal ions (Au(III), Ga(III), Fe(III), and Zn(II)) and nonionic surfactants in a high-concentration HCl solution by low-pressure-high performance liquid chromatography, with a low-flow-resistance polystyrene-based monolithic column [7]. In this work, the interactions between the metal ions and nonionic surfactant, i.e., polyoxyethylene nonylphenyl ether coated on the polymer monolith surface, were evaluated chromatographically.

In an actual CCFS process, two types of interactions between the metal ion and the foam surface are possible. One is a direct interaction between the metal ion and the surfactant layer on the foam. Alternatively, the compounds interact with the surfactant micelles in an aqueous region between the foams, after which, micelles capturing metals interact with the foam surface. When a hydrophobic reagent is used for the selective extraction of valuable metals, the latter situation will be observed in general. The evaluation of the interactions between the micelles and metal ions is essential for understanding the mechanism of the recovery process, in depth.

Capillary electrophoresis (CE) is an effective tool for evaluating the interaction between the compounds in the liquid phase [8-12]. Therefore, we employed CE to evaluate the interactions between the metals and micelles in the presence of hydrophobic extraction agents. In this study, we evaluate the interaction between palladium ion and anionic/nonionic micelles.

Palladium is one of the platinum group metals, which is of importance in various fields, such as catalysis [13-15], hydrogen storage [16], and metal plating [17,18]. Therefore, studies on palladium recovery from wastes are often reported [19-21]. Recently, \(N, N'-\text{dimethyl-}N, N'\text{-di-n-octyl-thiodiglycolamide} \) (MOTDA) was developed for the selective recovery of palladium(II) from platinum(IV) [22]. As a similar agent, \(N, N'-\text{dimethyl-}N, N'\text{-di-n-hexyl-thiodiglycolamide} \) (MHTDA, Fig. 1) was also developed and its application as an adsorbent was reported [23]. In addition, the selective recovery of palladium using MHTDA and nonionic surfactant was investigated in CCFS [24]. In this study, the interactions between the palladium ions and the anionic/nonionic micelles were evaluated with and without MHTDA. Throughout this study, a platinum(IV) chloride complex was used as a reference to evaluate the electrophoretic behavior of palladium(II) ions.

2. Experiment

2.1. Chemicals

MHTDA (brand name: Creastar Pd-EX), sodium dodecyl sulfate (SDS), hydrogen chloride, sodium chloride, palladium dichloride, and platinum tetrachloride were purchased from Wako Pure Chemical (Osaka, Japan). Polyoxyethylene mono-4-octylphenyl ether (POOPE, \(n \approx 10\), Fig. 1) was purchased from Tokyo Chemical Industry (Tokyo, Japan).

2.2. Apparatus and procedure

A commercial CAPI-3100 instrument (Otsuka Electronics, Osaka, Japan) with a fused-silica capillary of i.d. 0.050 mm (whole length: 50 cm; effective length: 38 cm; GL Sciences, Tokyo, Japan) was used. The separations were carried out with applied voltages of −8 or +8 kV at 25 °C, and the analytes were mainly detected by optical absorbance at 200-400 nm. The sample solution (PtCl\(_4\)/PdCl\(_2\) dissolved in 0.1 M HCl aqueous solution with 200-400 ppm for the each metal ion) was injected by a hydrodynamic method (\(\Delta H = 25 \text{ mm}, 30 \text{ s}\)).

3. Results and discussion

3.1. Interaction with micelles without MHTDA

The elements in the platinum group forms negatively charged chloride complexes in an acidic solution containing a high concentration of chloride anion [25,26]. The electrophoretic separation of platinum and palladium complexes in 0.1 M HCl with an application of −8 kV at an inlet is shown in Fig 2A. With the applications of −8 and +8 kV, the elution of the neutral analyte (acetone) was not observed within 40 min, because the use of acidic electrophoretic media suppressed the generation of electroosmotic flow (EOF). Therefore, both platinum and palladium chloride complexes migrated toward the outlet end mainly by their electrophoretic mobility only, i.e., the apparent electrophoretic mobility (\(\mu_{\text{app}}\)) was almost equal to the electrophoretic mobility (\(\mu_{\text{op}}\)) for each metal anion complex. Fig. 2A indicated that the platinum(IV) complex, in this case, has a larger electrophoretic mobility compared with that of the palladium(II) complex. In contrast with Fig. 2A, the elution order of platinum(IV) and palladium(II) was reversed in Fig. 2B, in which 0.1 M HCl containing 0.4 M NaCl was used as an electrophoretic medium. In a 0.1 M HCl aqueous solution, platinum(IV) forms PtCl\(_6\)^{2−} and palladium(II) mainly forms either PdCl\(_2\)^{2−} or PdCl\(_2\)^{2−} [25,26].
When the chloride ion concentration increased due to the addition of NaCl, the net negative charge for the palladium(II) chloride complex increased due to the enhancement of the PdCl$_4^{2–}$ formation and migration order was exchanged.

Fig. 3 shows the effect of the surfactant addition on the electrophoretic mobility of the palladium and platinum chloride complexes, and the relative difference in mobility ($\Delta \mu_{app, Pd-Pt}/\mu_{app, Pt}$). Electrophoretic media: 0.1 M HCl aqueous solution containing (A) MHTDA and (B) SDS. The critical micelle concentration in pure water for each surfactant is indicated in each figure. Other conditions are the same in Fig. 2.

### 3.2. Interaction with MHTDA in the presence of micelles

The effect of the MHTDA addition on the electrophoretic behavior of palladium(II) was investigated. As the electrophoretic media, 0.1 M HCl - 2 mM POOPE containing MHTDA were used. When 0.08 mM, 0.21 mM, or 0.24 mM MHTDA was added to the media, no palladium peak was observed in the electropherograms with an application of –8 kV, whereas the elution of platinum was clearly observed (data not shown). The application of +8 kV generated an electropherogram lacking both palladium and platinum peaks. This behavior indicated that $\mu_{app, Pd}$ (or $\mu_{app, Pt}$) was approximately zero, or negligible. MHTDA formed a neutral and the hydrophobic complex with palladium(II), and the complex was captured in the POOPE micelles. The electrophoretic migration velocity of the POOPE micelle was small and a peak of palladium was not observed in the electropherogram within 40 min.

The variation in electropherogram due to the MHTDA addition is shown in Fig. 4, using the electrophoretic media of 0.1 M HCl - 10 mM SDS aqueous solution. Although the variation in the migration time was observed, the
platinum(IV) chloride complex was detected as a single peak unaffected by the MHTDA addition except the higher MHTDA concentrations (>0.61 mM), i.e., slight tailing of the peak may indicate the slight generation of a species with a relatively low electrophoretic mobility. In the media containing SDS, palladium(II) clearly resulted in plural peaks with the MHTDA addition. For the detailed study, the relationship between the MHTDA concentration and relative difference in mobility of each peak to the platinum peak is shown in Fig. 5, and the difference UV spectrum ((spectrum at a peak top) – (spectrum at a front end)) for each peak is shown in Fig. 6. As shown in Fig. 6, the spectra of a, b, and e show $\lambda_{\text{max}}$ at ~225 nm. The addition of MHTDA of 0.08 and 0.13 mM resulted in peaks of c, d, f, and g. The spectra for these peaks were clearly different from those of a-b-e series, i.e., no absorbance peaks at 225 nm and the other absorbance peaks at 250 nm. The spectra of i, j, k, l, m, n, and p were almost comparable with those of c, d, f, and g. Therefore, these peaks will be categorized in the same group. In the spectrum of h, peaks at 225 and 250 nm were observed. Therefore, it will be predicted that these spectra were obtained by the overlapping these species. As shown in Figs. 5 and 6, three chemical species were found in the presence of MHTDA. However, further study is necessary for their identification.

### 3.3. Extraction of palladium to micelles in the presence of MHTDA

The solubility of the extraction reagent, MHTDA, in water is small and it will be captured in the micelles in the aqueous electrophoretic media. The electrostatic repulsion between the SDS micelles and the anionic chloride complex of palladium(II) suppresses the interaction between the complex and MHTDA in the SDS micelles. Therefore, the MHTDA-palladium complex is formed with the ligand exchange reaction of the palladium chloride complex with MHTDA slightly existing outside the SDS micelles.
In a case of POOPE micelles, the absence of electrostatic repulsion or the presence of weak electrostatic attractive force may result in the direct ligand exchange reaction with MHTDA inside of the micelles. Therefore, in the electrophoretic media containing POOPE, the MHTDA complex was captured rapidly in the POOPE micelles and resulted in the elimination of the peak. This result suggests that, in comparison with SDS, POOPE is a better surfactant for CCFS using MHTDA for the recovery of palladium.

### 4. Conclusion

In this study, the interactions between palladium(II) and MHTDA in the presence of the micelles were investigated. In the electrophoretic media containing SDS micelles, the three chemical species were found in electropherogram, and two species would be categorized in the same group. The use of SDS will be effective for the study of detailed mechanism of palladium-MHTDA complexes formation and their extraction in the micelles. In addition, it was revealed that POOPE was a suitable surfactant for CCFS using MHTDA to recover palladium compared with SDS. However, this condition is not suitable for the study of the complex formation and the extraction procedure due to the less electrophoretic mobility of the POOPE micelle and less electroosmotic mobility under a highly acidic condition. The use of a capillary with surface modification to generate a stable electroosmotic flow will be effective for further studies on the interaction between the palladium-MHTDA complexes and POOPE micelles.

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