Slug Flow Extraction and Separation of Nickel and Cobalt with D2EHPA

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Slug flow is one of the typical flow patterns in microtube. The slug flow provides high mass transport due to the internal circulation within each segment. Additionally, it can precisely control the contact time between two phases. In this study, the slug flow was applied and discussed for the extraction and separation of Ni^{2+} and Co^{2+} from an aqueous solution into a cyclohexane phase, which contained di-(2-ethylhexyl) phosphoric acid (D2EHPA) as an extraction reagent. The extraction time of the maximum separation factor becomes longer with decreasing the flow velocity. These results suggest that the separation with high separation factor is available by adjusting of the extraction time.

1. Introduction

A liquid-liquid extraction process is widely used in the separation of rare metals, but conventional liquid–liquid extraction equipment (e.g., a continuous mixer–settler) tends to be quite large, as it requires a long time for phase separation after mixing the aqueous and organic solutions. In particular, the particle diameter of the dispersed phase has a large influence on the mass transfer rate. The dispersed phase coalesces and the particle size increases when it moves in the extraction column. In addition, the dispersed phase disperses axially as it travels through the extraction column. These phenomena reduce the mass transfer rate, and thus, design methods for such apparatus are complicated. This has led to increased interest in the use of slug flow (the alternating flow of two or more phases through a tube), [1-3] which offers a number of advantages in liquid–liquid extraction. Cobalt and nickel are important elements for charge/discharge devices such as lithium ion batteries [4], the demand for which has increased remarkably in recent years. This study explores the possibility of using slug flow to extract Cobalt and nickel ions (Co^{2+} and Ni^{2+}) from an aqueous solution into an organic phase consisting of cyclohexane with di-(2-ethylhexyl)phosphoric acid (D2EHPA) as an extraction reagent. This organic phase was selected because it is easily separated from the aqueous phase and has a high ability to extract alkaline metal ions [5].

2. Experimental

2.1 Reagents

Aqueous cobalt and/or nickel solutions were prepared by dissolving cobalt chloride (Wako Pure Chemical Industries Ltd. Japan) and / or nickel chloride (Wako Pure Chemical Industries Ltd. Japan) in deionized water. The organic phase was prepared by dissolving 40, 100 and 200 mM of D2EHPA (Tokyo Chemical Industries Ltd, Japan) was dissolved in cyclohexane as an organic solvent. Prior to be used, it was substituted H^+ of D2EHPA to Na^+ by adding 10 mM aqueous solution of sodium hydroxide (Wako Pure Chemical Industries Ltd. Japan).

2.2 Experimental apparatus and procedures

2.2.1 Batch extraction experiments

Equal volumes of the aqueous and organic solutions were poured into a snap-cap vial and agitated in at thermostatic batch at 25°C until equilibrated (more than 18 h). The concentrations of cobalt and Nickel in the aqueous phase were determined by atomic adsorption spectrophotometry and the pH of the aqueous phase was measured using a pH meter.

2.2.2 Continuous extraction experiments

Continuous extraction by slug flow was performed using the apparatus shown in Figure 1. Each solution was fed into the Y-junction at a constant total flow rate of 0.25 - 0.75 mL/min using a syringe pump and the two phases were then passed through the microtube. As the extraction time corresponds to the time needed for the liquids to flow from the Y-junction to the end of the microtube, the extraction times ere varied by simply adjusting the length of the microtube and flow rate. Continuous extraction experiment was conducted under same volume of the organic solution and the aqueous solution. All experiments were conducted three times using transparent polytetrafluoroethylene (PTFE) (i.d.: 1mm) microtube so that the flow pattern of liquid could be observed. The exhausted solution was collected in an 8-mm-diameter class receiver, which reduced the interface area between the aqueous and organic phases, causing them to instantly separate. As a preliminary experiment, the amount of extracted ions in the receiver was confirmed to be negligible when compared with the amount in the

Figure 1 An illustration of continuous extraction experiment.

PTFE tube. After testing, the Co^{2+} and Ni^{2+} concentration in the exhausted aqueous phase was analyzed by atomic adsorption spectrophotometry. The details of the procedure are described elsewhere [6].
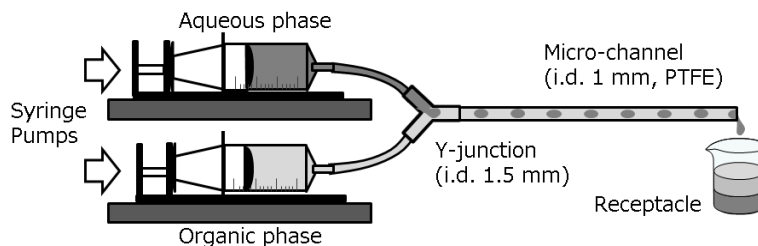
3. Results and Discussion

3.1 Distribution properties of Co^{2+} and Ni^{2+}

Distribution characteristics of Co^{2+} and Ni^{2+} in various concentrations of D2EHPA in cyclohexane were determined by batch experiments. Figure 2 shows the distribution characteristics of Co^{2+} and Ni^{2+} when D2EHPA concentrations are 40, 100 and 200 mM. The initial concentration of Co^{2+}

and Ni^{2+} in the aqueous phase was 1 mM, and an aqueous solution of a single component metal ion was dissolved in the experiment. As extraction progresses, H^+ of D2EHPA moves from the oil phase to the aqueous phase and the pH of the aqueous phase decreases. Here, a part of H^+ of D2EHPA was substituted in advance with Na^+ (0 to 60 mol%) before the experiment. Extraction rate E is defined as,

$$E = \frac{c_0 - c}{c_0} \qquad (1)$$

Where C is metal concentration of the aqueous phase and C_0 is feed concentration. When the concentration of D2EHPA is high (200 mM), the distribution curves of Co^{2+} and Ni^{2+} show that the extraction rate increases as the pH of the aqueous phase is higher at pH 3.5-4.5. Co^{2+} is located on the

Figure 2 Distribution Curves of Co^{2+} and Ni^{2+}. Closed key; Co^{2+}, open key; Ni^{2+}. Concentrations of Co^{2+} and Ni^{2+} are 1.0 mM. Concentration of D2EHPA; circle is 40 mM, square is 20 mM, triangle is 100 mM.

side where pH is lower than Ni^{2+}. When the concentration of D2EHPA was 100 mM, the distribution curve of Ni^{2+} moved about 1 in the direction of higher pH. In D2EHPA showing high pH, that is, a high substitution rate of Na^+, the extraction rate became small and the maximum value was found. When the

concentration of D2EHPA was 100 mM, the above tendency became remarkable. It was suggested that Co^{2+} can be selectively extracted at pH > 5. This indicates that highly selective extraction of Co^{2+} is possible by appropriately selecting the concentration of D2EHPA and the Na substitution rate of D2EHPA.

Figure 3 shows the distribution curve by D2EHPA for a mixed solution of Co^{2+} and Ni^{2+}. As in the experiment Figure 2, a batch extraction experiment was conducted by replacing a part of H^+ in D2EHPA with Na^+. The concentration of D2EHPA was 200 mM, the concentrations of Co^{2+} and Ni^{2+} were 0.5 and 1.0 mM. When the metal ion concentration was more dilute, the distribution curve was shifted to the lower pH side. Therefore, the extraction rate of Co^{2+} was higher than that of Ni^{2+} at the same pH. Figure 4 shows the distribution curve of a mixed solution of Co^{2+} and Ni^{2+} when the concentration of D2EHPA is 40 mM. Ni^{2+} was
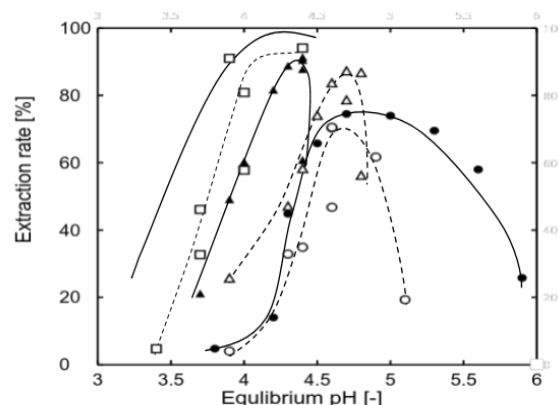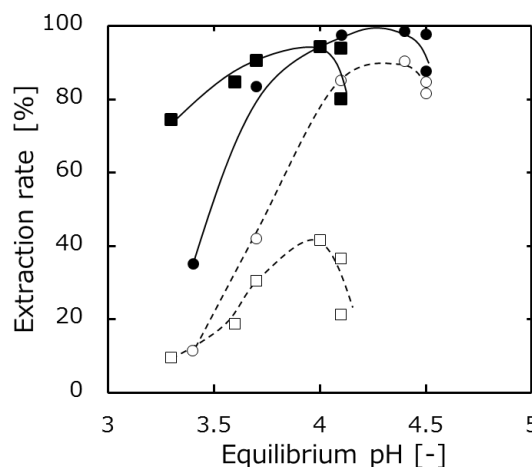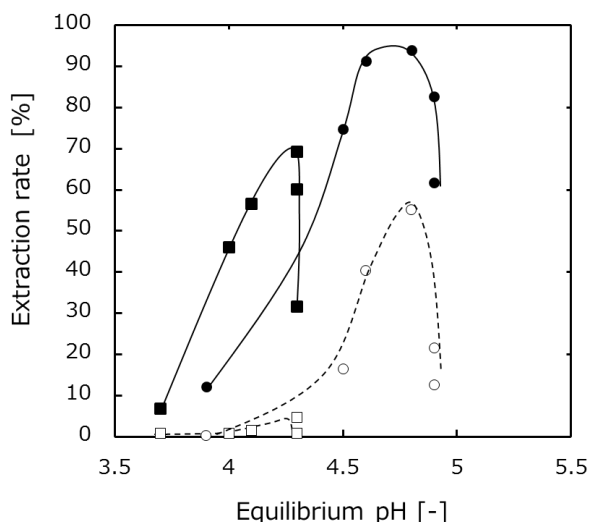

Figure 3 Distribution Curves of Co^{2+} and Ni^{2+}. Closed key; Co^{2+}, open key; Ni^{2+}. Concentrations of D2EHPA is 200 mM. Initial concentration of Co^{2+} and Ni^{2+}; circle is 0.5, mM, square is 1.0 mM.

scarcely extracted when pH < 4.3 and only Co²⁺ was selectively extracted.The continuous extraction experiments were carried out under the codition; D2EHPA concentarion was 40 mM, each concentarion of Co²⁺ and Ni²⁺ was 1.0 mM.

3.2 rate experiment

The overall volumetric mass transfer coefficient $k_L a$ is one of the parameters used to evaluate the extraction rate and can be obtained as follows. [7] First, the mass transfer rate N_A [mol/(L·s)] is determined using:

$$N_A = -\frac{dc}{dt} = -k_L a(C - C^*) \qquad (2)$$

where t is the extraction time [s] and C^* is the metal ion concentration [M] in the aqueous phase at extraction equilibrium. Integration of Eq. (2) gives:

$$-\ln(C - C^*) = k_L a t + A \qquad (3)$$

Substitution of Eq. (1) into Eq. (3) gives:

$$-\ln\left(1 - \frac{E}{E^*}\right) = k_L a\, t + A' \qquad (4)$$

where E^* are the extraction efficiencies at equilibrium.

$$E^* = \frac{C_0 - C^*}{C_0} \qquad (5)$$

A and A' are constants and C_0 is the feed concentration. As Eq. (5) shows that –ln (1 – E/E*) is a linear function of extraction time t, experimental data for the extraction efficiency and extraction time were used to plot –ln(1 – E/E*) against t. From the gradient of the linear plot, $k_L a$ was obtained.

The continuous extraction experiments by the slug flow were conducted under various

Figure 4 Distribution Curves of Co²⁺ and Ni²⁺. Closed key; Co²⁺, open key; Ni²⁺. Concentrations of D2EHPA is 40 mM. Initial concentration of Co²⁺ and Ni²⁺; circle is 0.5, mM, square is 1.0 mM.
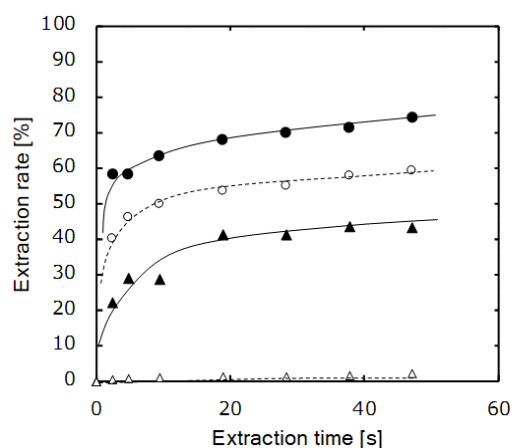

Figure 5 Continuous extraction of mono metal component. Closed mono-component, open key; mixture of Co²⁺ and Ni²⁺. Concentration of the aqueous feed solution; 1.0 mM. D2EHPA concentration; 40 mM. Linear velocity; 0.021 m/s. Circle; Co²⁺, triangle; Ni²⁺.

feed concentration and linear velocity. The relationship between extraction time and extraction rate is shown in Figure 5. Figure 5 shows the extraction rate for the single metal ion component of Co²⁺ and Ni²⁺. Each Co²⁺ and Ni²⁺ were quickly extracted just after the start of the extraction and gradually

approached the distribution equilibrium (cobalt; 75%, nickel; 65%, See Figure 2). The extraction experiment of the mixed solution of Co^{2+} and Ni^{2+} was carried out under the same conditions. The extraction rate of Co^{2+} decreasd somewhat with the influence of coexisting Ni^{2+}. On the cotrary, rate of Ni^{2+}extraction dramatically decreased with the influence of Co^{2+}. Li et al. report that the affinity of D2EHPA and Co^{2+} is larger than that of Ni^{2+} in an organic solvent. We think that this result affects difference rate of extraction of Co^{2+} and Ni^{2+}. The mass transfer capacity coefficients of Co^{2+} and Ni^{2+} were calculated From the experimental results. Figure 6 shows the relationship between the Reynolds number

Figure 6   Effect of *Re* on volumetric mass transfer coefficient of Co^{2+} and Ni^{2+}. ● ; Co^{2+}, ○ ; Ni^{2+}

(Re, $=du\rho/\mu$, d; diameter of tube, u; liner flow rate, ρ; density of fluid, μ; viscosity of fluid) and the mass transfer capacity coefficient expressed by physical property values of the aqueous solution by experiments with different linear and oil phase linear velocities. The mass transfer capacity coefficient increased linearly with increasing of Reynolz number. We consider that the circulation flow in each segment of the oil phase and the aqueous phase increases and the extraction speed is increased as the linear velocity of the fluid increases,. When the linear flow velocity is small, the mass transfer capacity coefficient of nickel is close to zero. Therefore, high selective separation Co^{2+} and Ni^{2+} is available by the slug flow extraction.
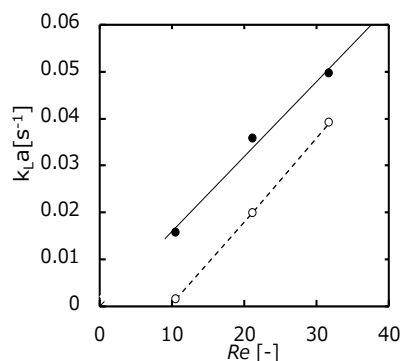
Finary, Purity and separation facotor $\beta_{Co/Ni}$ is calculated for the extraction of mixed Co^{2+} and Ni^{2+}solution. The time dependence of the separation factor $\beta_{Co/Ni}$ is shown in Figure 7. $\beta_{Co/Ni}$ is defined as

$$\beta_{Co/Ni} = (\frac{C_{0,Co}-C_{Co}}{C_{Co}})/(\frac{C_{0,Ni}-C_{Ni}}{C_{Ni}}) \quad (6)$$

The maximum values of $\beta_{Co/Ni}$ were 38 at 20 s when liner velocity was 0.032 m・s^{-1}, 38 at 40 s when liner velocity was 0.021 m・s^{-1}, and 80 at 40 s when liner velocity was 0.011 m・s^{-1}. The difinition of cobalt purity is ($C_{Co}^{2+} / C_{Co}^{2+}+ C_{Ni}^{2+}$)) in the organic phase. The relationship between cobalt purity and extarction time is shown in Figure 8. The cobalt purity decreased with increasing of extration time. At just after the starting extraction, the exctraction of Co^{2+} is more rapid than Ni^{2+}, the cobalt purity was near to 1.0. The cobalt purity increased with decraesing of the flow linear velocity. The linear velocity was smaller, the ratio of volmetric
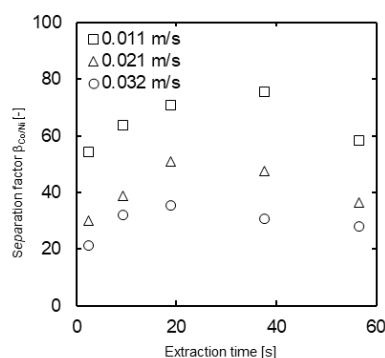

Figure 7 Time dependence of separation factor $\beta_{Co/Ni.}$ Concentration of the aqueous feed solution; 1.0 mM. D2EHPA concentration; 40 mM.

mass transfer coefficient of Co^{2+} and Ni^{2+} is larger. These results suggests that the extraction by the slug flow can separate ions with high selectivity with controlling linear velocity and extraction time.

4. Conclusion

In this study, extraction and separation of Co^{2+} and Ni^{2+} by liquid-liquid extraction using a slug flow were investigated. The main conclusions drawn from this study are as follows:

(1) The distribution curves of Co^{2+} and Ni^{2+} were depended the concentration of the ions and the extract reagent (D2EHPA), and Na substitution rate of D2EHPA.

(2) The extraction rate of Co^{2+} which had high selectivity became slightly smaller even when Ni^{2+} coexisted. On the contrary, the extraction rate of Ni^{2+} dramatically decreased with coexisting of Co^{2+}.

(3) The overall mass transfer coefficient of Co^{2+} and Ni^{2+} increases linearly with increasing of *Re*.

(4) The purity and separation factor of Co^{2+} increased with decreasing linear flow rate and showed the maximum value depending on extraction time.
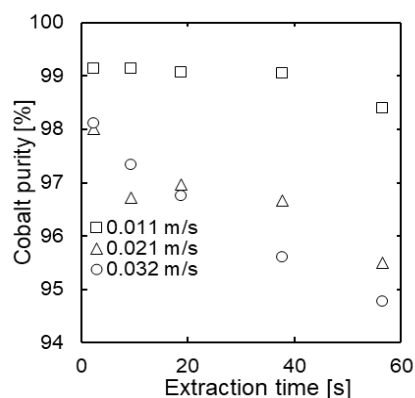

Figure 8 Time dependence of cobalt purity. Concentration of the aqueous feed solution; 1.0 mM. D2EHPA concentration; 40 mM.

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