

Flow System for Mutual Separation of Aluminum(III), Gallium(III) and Indium(III) Used Forward- and Back-Extraction Process

Saori Osanai, Masanobu Mori, Atsuko Tsunoda and Hideyuki Itabashi*

Graduate School of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan

Abstract

A continuous flow system for mutual separation of aluminum(III), gallium(III) and indium(III) was developed based on 4,4,4-trifluoro-1-(2-thientl)-1,3-butanedione (TTA) extraction. The proposed flow system has two extraction coils, a forward-extraction coil and a back-extraction coil. In the forward-extraction coil, gallium(III) and indium(III) are extracted into the organic phase while aluminum(III) is hardly extracted. In the back-extraction coil, indium(III) is back-extracted into the aqueous phase while gallium(III) remains in the organic phase. Consequently, when a sample solution is introduced into the system, aluminum(III), gallium(III) and indium(III) are separated each other. The effects of the length of the extraction coils and the flow rate of the pump on the separation efficiency were examined. The proposed flow system with extraction coils, 10 m in length for forward-extraction and 1 m in length for back-extraction, enabled the quantitative separation of aluminum(III), gallium(III) and indium(III).

Keywords Solvent extraction, kinetic separation, aluminum(III), gallium(III), indium(III), continuous flow system

1. Introduction

Mutual separation of aluminum(III), gallium(III) and indium(III) becomes more and more important from industrial view points because these metals are widely used as low materials of many industrial products such as containers, semiconductors and electronic devices. TTA (4,4,4-trifluoro-1-(2-thientl)-1,3-butanedione) extraction is one of the most useful method for group separation of these metal ions from many kinds of matrixes [1]. However, the mutual separation of these metal ions by TTA extraction in the equilibrium state is a difficult task, because the extraction constants (K_{ex}) for aluminum(III) ($= 10^{-5.23}$), gallium(III) ($= 10^{-7.57}$) and indium(III) ($= 10^{-4.34}$) are too close to separate them quantitatively [2].

On the other hand, it is well known that the labilities of these metal ions are much different from each other. For example, the water-exchange rate constants (k_{H_2O}) for their aqua complex ions are aluminum(III) $= 1 \text{ s}^{-1}$, gallium(III) $= 10^3 \text{ s}^{-1}$, and indium(III) $= 5 \times 10^6 \text{ s}^{-1}$, respectively [3]. The difference in the lability indicates the possibility of the quantitative separation of these metal ions in a nonequilibrium state because the extraction rate of metal ions depends on their labilities.

From the point of view, in our previous work, kinetically controlled separation of cadmium(II) from zinc(II) by dithizone (3-mercpto-1,5-diphenylformazan) extraction were tested [4]. In the equilibrium state, mutual separation of cadmium(II) and zinc(II) by dithizone extraction is difficult because the extraction constants for both metal ions are almost the same [2]. However, in a nonequilibrium state, in which the extractability of metal

ions depends on the extraction rate, mutual separation of cadmium(II) and zinc(II) was attained because the extraction rate of cadmium(II) was larger than that of zinc(II). Furthermore, it was found that the back-extraction rate of cadmium(II)-dithizone complex was much larger than that of zinc(II) complex [5,6], the results indicated the possibility of the quantitative separation of cadmium(II) from zinc(II) by dithizone extraction if the back-extraction took place followed by the forward-extraction. However, the two-stage extraction procedure will be somewhat tedious because it is necessary to transfer the solution into another separatory funnel. Moreover, the kinetic separation by batch procedure will be a laborious technique because the regulation of the extraction time including a separation procedure seems to be difficult.

On the other hand, a flow injection technique has been widely used for analytical purposes [7]. A flow injection technique makes it possible to develop not only automatic systems but also precision methods. Solvent extraction using a flow injection technique has been also developed and it has been used to the determination of some extractive species such as surfactants [8-13]. However, the extractive flow technique has hardly been used for mutual separation of metal ions. If the extractive flow system equipped with both forward- and back-extraction processes is developed, it would to be a useful system for the mutual separation of metal ions. Further, kinetic separation would be easily performed by the extractive flow system, because desired extraction time is obtained by only adjusting the extraction coil length and the flow rate of the pump.

From the point of view, in our previous study, the extractive

flow system for the mutual separation of cadmium(II) and zinc(II) was developed[14]. Although the system allowed to separate of two kinds of metal ions, i.e., cadmium(II) and zinc(II), simultaneous separation of three kinds of species has not been performed. In this paper, a continuous flow system for the separation of three kinds of metal ions, i.e., aluminum(III), gallium(III) and indium(III) was developed based on forward- and back-extraction with TTA, and the feasibility of the proposed system was described.

2. Experimental

2.1 Reagents

4,4,4-Trifluoro-1-(2-thientl)-1,3-butanedione (TTA) was obtained from Dojin Chemical Co., and was dissolved in benzene. Acetate and fluoride solutions were prepared by dissolving appropriate amount of ammonium acetate and ammonium fluoride (Wako Chemicals) in water. The water used to prepare the reagents was obtained from a Milli-Q water-purification system (Millipore Co.). Aluminum(III), gallium(III) and indium(III) solutions were prepared by dilution of 1000 ppm standard solutions obtained from Wako Pure Chemicals. PTFE chips (*ca.* $0.4 \times 0.4 \times 0.1$ mm) used as packing materials were made by cutting a PTFE tube.

2.2 Apparatus

Two double-plunger pumps (Sanuki Kogyo, DMX-2000) were used for propelling sample and reagent solutions. A phase separator (Sanuki Kogyo) with porous PTFE membrane filter and an air-trapping system (Sanuki Kogyo, AD-2) were used for the separation of organic and aqueous phases. A Shimadzu (Model ICP-1000IV) inductively coupled plasma atomic emission spectrometer (ICP-AES) and A Hitachi (Model Z-6100 and 170-50A) atomic absorption spectrometer (AAS) equipped with a hollow cathode lamp (Hamamatsu Photonics) was used for the determination of metal ions. A Fisher Scientific pH meter (Accumet pH meter 15) was used for pH measurements. PTFE tubes (ϕ 2 mm) packed with the PTFE chips were used as forward- and back-extraction coils[13].

2.3 Procedure

2.3.1 Measurements of extractability of aluminum(III), gallium(III) and indium(III) in forward-extraction processes

For the measurement of the forward-extractability, an aqueous solution containing 1×10^{-4} mol dm⁻³ aluminum (III), gallium (III) and indium (III), 1×10^{-2} mol dm⁻³ ammonium fluoride and 0.1 mol dm⁻³ acetate buffer (pH = 4.0) was propelled by a

double-plunger pump. A benzene solution containing 0.1 mol dm⁻³ of TTA was also propelled by the double-plunger pump. The solutions were merged through a T-connector and then introduced into an extraction coil. After the aqueous phase was separated from the organic phase by a phase separator, the metal's concentration in the aqueous phase was measured by ICP-AES or AAS. The above procedures were conducted at various flow rate and various coil length. The reaction (extraction) time was calculated as the resistance time of the solution within the extraction coil.

2.3.2 Measurements of extractability of gallium(III) and indium(III) in back-extraction processes

For the measurement of the back-extractability of gallium(III) and indium(III), an aqueous solution containing 0.1 mol dm⁻³ nitric acid was propelled by a double-plunger pump. A benzene solution containing 0.1 mol dm⁻³ TTA, 1×10^{-4} mol dm⁻³ gallium(III) and indium(III) was also propelled by the double-plunger pump. Other procedures were the same to the forward-extraction process.

2.3.3 Continuous flow separation of aluminum(III), gallium(III) and indium(III)

Schematic diagram of the proposed system is shown in Fig.1.

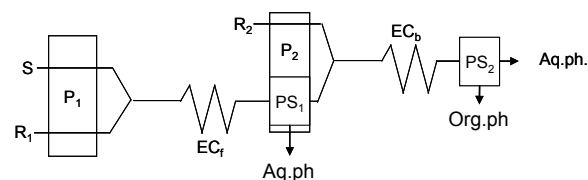


Fig. 1 Continuous flow system for separation of aluminum(III), gallium(III) and indium(III).

S: sample solution, R₁: benzene solution containing 0.1 mol dm⁻³ TTA ([TTA]_{org} = 0.1 mol dm⁻³), R₂: 0.1 mol dm⁻³ nitric acid solution, EC_f: forward-extraction coil packed with PTFE chips (ϕ 2mm, 10m in length), EC_b: back-extraction coil packed with PTFE chips (ϕ 2mm, 1m in length), P₁: double plunger pump (1.25 cm³ min⁻¹), P₂: double plunger pump (1.25 cm³ min⁻¹), PS₁: phase separator used PTFE membrane filter, PS₂: phase separator used PTFE membrane filter, Aq.ph: Aqueous phase, Org.ph.: Organic phase.

A sample solution containing aluminum (III), gallium (III) and indium (III), 1×10^{-2} mol dm⁻³ ammonium fluoride and 1×10^{-1} mol dm⁻³ acetate buffer (pH = 4.0) was propelled by the double plunger pump(P₁). A benzene solution containing 0.1 mol dm⁻³ TTA was also propelled by the pump (P₁). The solutions were

merged through a T-connector and then introduced into the forward-extraction coil packed with PTFE chips (EC_f, ϕ 2 mm, 10 m in length). The organic phase was separated from the aqueous phase with the phase separator (PS₁) and the organic phase was pumped into the flow line. An aqueous solution, of which the concentration was adjusted to 0.1 mol dm⁻³ nitric acid solution, was also propelled by the double plunger pump (P₂) and merged with the organic phase. The mixture was introduced into the back-extraction coil packed with PTFE chips (ϕ 2 mm, 1 m in length) and then the aqueous phase was separated from the organic phase with the phase separator (PS₂).

The aluminum (III), gallium (III) and indium (III) concentrations in the aqueous phase were measured by ICP-AES or AAS. All experiments were carried out at room temperature (*ca.* 293 K).

3. Results and Discussion

3.1 Separation of gallium(III) and indium(III) from aluminum(III) in the forward-extraction process

From the comparison of the water-exchange rate constants ($k_{\text{H}_2\text{O}}$) for their aqua complexes, the extraction rates of these metal ions are estimated to be larger in the following order; indium(III) > gallium(III) > aluminum(III). Therefore, in the first separation of the proposed system, indium(III) and gallium(III) have to be extracted quantitatively into the organic phase in the EC_f shown in Fig.1 while large amount of aluminum(III) has to be remained in the aqueous phase. However, as shown in Fig. 2, more than 20% of aluminum(III) was extracted into the organic phase when the extraction was taken place in the conditions of quantitative-extraction of indium(III) and gallium(III), i.e., the concentration of TTA in the organic phase was 0.1 mol dm⁻³, pH of the aqueous phase was 4.0.

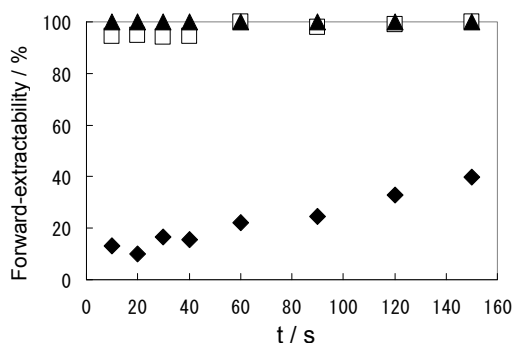
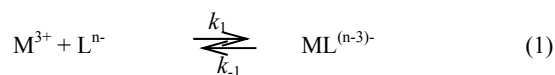


Fig. 2 Forward-extractability of aluminum(III) (◆), gallium(III) (□) and indium(III) (▲) in the absence of masking reagents. $[\text{Al}^{\text{III}}] = [\text{Ga}^{\text{III}}] = [\text{In}^{\text{III}}] = 1 \times 10^{-4}$ mol dm⁻³, pH = 4.0, $[\text{TTA}]_{\text{org}} = 0.1$ mol dm⁻³.

To attain the above purposes, the adding of a masking reagent was examined. If the reaction of a metal ion (M^{3+}) and the masking reagent (L^n) proceeds as follows, the stability constant (K_{ML}) is defined as



$$K_{\text{ML}} = \frac{k_1}{k_{-1}} \quad (2)$$

where k_1 and k_{-1} denote the forward- and backward-rate constants of reaction (1). In the presence of the masking reagent, the extraction rate of the metal ion depends on the k_{-1} value because the extraction proceeds followed by the reaction between TTA anion and M^{3+} which is provided by the dissociation of $\text{ML}^{(n-3)-}$. Therefore, adding the masking reagent with $K_{\text{ML}}^{\text{Al}} > K_{\text{ML}}^{\text{Ga}}, K_{\text{ML}}^{\text{In}}$ leads to expansion of the deference in the extraction rate between aluminum(III) and gallium(III) (or indium(III)), because the k_{-1} value of aluminum(III) becomes much smaller than that of gallium(III) and indium(III).

K_{ML} values for some complexing reagents are summarized in Table 1 [15]. Among them, F⁻ satisfies the above conditions. Therefore, F⁻ was selected as the masking agent.

Table 1 Stability constants of aluminum(III), gallium(III) and indium(III) complexes

Masking reagents	log K_{ML}^{a}		
	Al ^{III}	Ga ^{III}	In ^{III}
CyDTA	18.63	22.91	28.74
EDTA	16.13	20.27	24.95
NTA	9.5	13.6	16.9
oxalic acid	6.1	6.45	5.30
SCN ⁻	0.42	2.15	3.15
F ⁻	6.11	4.49	3.75

a. A. E. Martel and R. M. Smith "Critical Stability Constants", Plenum Press, New York, 1974.

CyDTA, trans-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid; EDTA, ethylenediamine-*N,N,N',N'*-tetraacetic acid; NTA, nitrilotriacetic acid

The forward-extractabilities of aluminum(III), gallium(III) and indium(III) in the presence of F⁻ are shown in Fig. 3. For the extraction time within 150 s, the extractability of aluminum(III) was extremely low while that of indium(III) was about 100%. For gallium(III), the extractability increased with

increasing in the extraction time, and then quantitative extraction was attained at 150 s. Consequently, the separation of gallium(III) and indium(III) from aluminum(III) in the forward-extraction process becomes possible by adding F^- as masking agent.

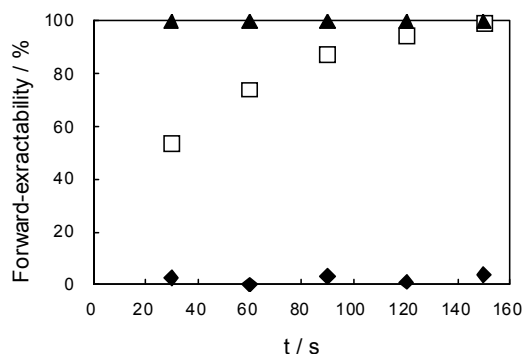


Fig. 3 Forward-extractability of aluminum(III) (◆), gallium(III) (□) and indium(III) (▲) in the presence of F^- .

$[Al^{III}] = [Ga^{III}] = [In^{III}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[F^-] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $pH = 4.0$, $[TTA]_{org} = 0.1 \text{ mol dm}^{-3}$.

To obtain the optimal conditions, the effect of flow rate on the forward-extraction process was examined. The results obtained by the systems with 3 m, 5 m, 8 m or 10 m extraction coils are shown in Fig. 4. Although aluminum(III) was not extracted into the organic phase in any conditions, the extractability of gallium(III) and indium(III) gradually decreased with increasing in the flow rate. In the case of continuous flow separation, fast flow rate provides the system with high throughput. Therefore, the optimal flow rates for the forward-extraction are as follows: $0.44 \text{ cm}^3 \text{ min}^{-1}$ for 3 m extraction coil length, $0.62 \text{ cm}^3 \text{ min}^{-1}$ for 5 m extraction coil length, $0.90 \text{ cm}^3 \text{ min}^{-1}$ for 8 m extraction coil length and $1.25 \text{ cm}^3 \text{ min}^{-1}$ for 10 m extraction coil length, respectively.

3.2 Separation of indium(III) from gallium(III) in the back-extraction process

In our previous paper described about the separation of cadmium(II) from zinc(II) [5-6], it was indicated that the back-extraction was useful method for the separation of labile metal ions from inert ones, because the back-extraction rate of the labile metal ions became much larger than that of inert ones. For the separation of indium(III) from gallium(III), lability of indium(III) is much larger than that of gallium(III), indium(III) will be back-extracted into the aqueous phase while gallium(III) will be remained in the organic phase.

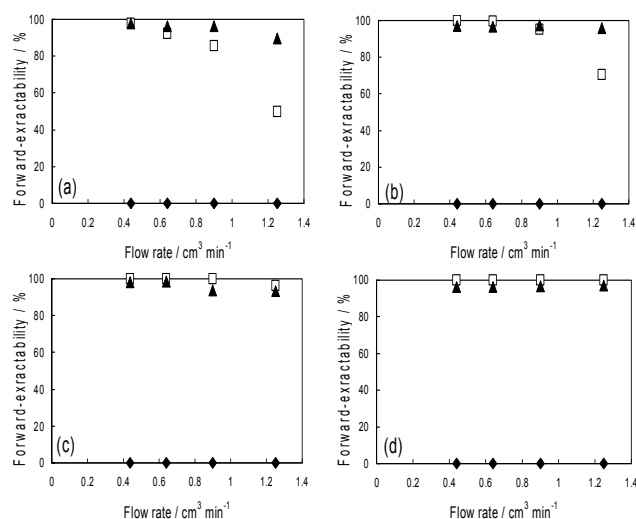


Fig. 4 Effect of flow rate on the forward-extractability of aluminum(III) (◆), gallium(III) (□) and indium(III) (▲).

$[Al^{III}] = [Ga^{III}] = [In^{III}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[F^-] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $pH = 4.0$, $[TTA]_{org} = 0.1 \text{ mol dm}^{-3}$, extraction coil length: (a) 3m, (b) 5m, (c) 8m and (d) 10m.

The effect of flow rate on the back-extraction was examined. A 0.1 mol dm^{-3} nitric acid solution was used as the aqueous phase, because gallium(III) was back-extracted when the solutions of pH lower than 1 were used as the aqueous phase. The results are shown in Fig.5. The extraction rate of indium(III) was large, so indium(III) was quantitatively back-extracted into the aqueous phase by using the 1 m PTFE tube as the back-extraction coil. On the other hand, gallium(III) was hardly back-extracted under the experimental conditions. When the systems with other extraction coil length were used, quantitative separation could be attained. Therefore, it was found that the back-extraction was a useful technique for the mutual separation of gallium(III) and indium(III).

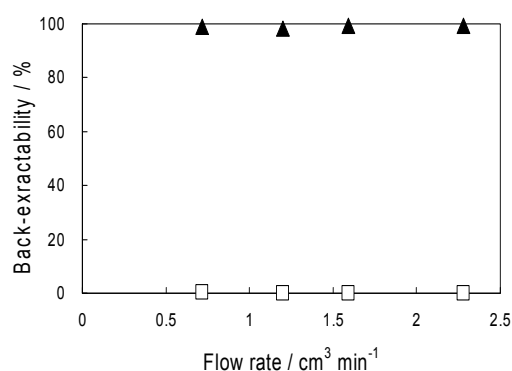


Fig. 5 Back-extractability of gallium(III) (□) and indium(III) (▲).

$[Ga^{III}]_{org} = [In^{III}]_{org} = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[TTA]_{org} = 0.1 \text{ mol dm}^{-3}$, aqueous phase: 0.1 mol dm^{-3} nitric acid, extraction coil length: 1 m.

3.3 Separation of aluminum(III), gallium(III) and indium(III)

By using the continuous flow system shown in Fig. 1, flow through separation of aluminum(III), gallium(III) and indium(III) was performed. The results are shown in table 2, where recovery % means as follows: Al(III) = (concentration of Al(III) in the aqueous phase after through PS₁) / (concentration of Al(III) in the sample solution) × 100, Ga(III) = (concentration of Ga(III) in the organic phase after through PS₂) / (concentration of Ga(III) in the sample solution) × 100, In(III) = (concentration of In(III) in the aqueous phase after through PS₂) / (concentration of In(III) in the sample solution) × 100. As summarized in Table 2, the recovery of each metal ion was about 100%, which indicated the feasibility of the system as the continuous flow method for the mutual separation of aluminum(III), gallium(III) and indium(III).

Table 2 Recovery of each metal ion through the system shown in Fig. 1

Metal concentration in the sample solution/mol dm ⁻³			Recovery /%		
[Al ^{III}]	[Ga ^{III}]	[In ^{III}]	[Al ^{III}]	[Ga ^{III}]	[In ^{III}]
1 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	>99.9	>99.9	>99.9
1 × 10 ⁻⁴	2 × 10 ⁻⁵	2 × 10 ⁻⁵	>99.9	>99.9	99.5
1 × 10 ⁻⁴	5 × 10 ⁻⁵	5 × 10 ⁻⁵	>99.9	>99.9	98.2
1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	>99.9	>99.9	>99.9
5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	97.3	>99.9	>99.9
5 × 10 ⁻⁴	2 × 10 ⁻⁵	2 × 10 ⁻⁵	97.6	>99.9	99.9
5 × 10 ⁻⁴	5 × 10 ⁻⁵	5 × 10 ⁻⁵	>99.9	>99.9	98.6
5 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	99.4	>99.9	97.8
1 × 10 ⁻³	1 × 10 ⁻⁵	1 × 10 ⁻⁵	>99.9	>99.9	>99.9
1 × 10 ⁻³	2 × 10 ⁻⁵	2 × 10 ⁻⁵	>99.9	>99.9	99.8
1 × 10 ⁻³	5 × 10 ⁻⁵	5 × 10 ⁻⁵	98.1	>99.9	>99.9
1 × 10 ⁻³	1 × 10 ⁻⁴	1 × 10 ⁻⁴	>99.9	>99.9	>99.9

4. Conclusion

A continuous flow system for the separation of aluminum(III), gallium(III) and indium(III) was developed based on the forward- and back-extraction processes with TTA. The proposed system enabled the quantitative separation of aluminum(III), gallium(III) and indium(III). The method would be applied to the separation of other metal ions with the difference in lability. Since the proposed method is simple and rapid, it would be a useful tool for the mutual separation of metal ions.

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