Unique Separation Based on Extraction Kinetics Using a Liquid-liquid Countercurrent Centrifugal Contactor with Taylor Vortices

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We performed a unique separation based on extraction kinetics using a liquid-liquid countercurrent centrifugal contactor that induces Taylor-Couette (TC) flow. Conventional extraction systems typically involve a mixer-settler extractor, which relies on an equilibrium being established. In the case of TC flow, species with faster extraction kinetics can be extracted more efficiently than those with slower kinetics, due to the countercurrent contact of the organic and aqueous phases. In this study, the separation of Fe(III) and Y(III) was achieved by using di(2-ethylhexyl) phosphoric acid (D2EHPA), for which the extraction kinetics are fast forY(III) but slow for Fe(III). Under equilibrium conditions, Fe(III) is more readily extracted than Y(III), but during countercurrent operation with TC flow, the order of extractability is reversed, with Y(III) being more readily extracted than Fe(III). For the condition where the metal ion concentrations are higher than the ligand concentration, which is a more competitive extraction condition for metal ions, the distribution ratio (*D*) values for both Y(III) and Fe(III) were decreased, but the selectivity for Y ($SF_{\mathrm{Y/Fe}} = D_{\mathrm{Y(III)}}/D_{\mathrm{Fe(III)}}$) increased. Thus, solvent extraction with TC flow may allow the design of effective, efficient separation processes.

1. Introduction

Solvent extraction is one of the most reliable and effective methods for separation of metal ions in solution. Designing ligands with high selectivity for specific ions is important, and for large-scale operations, the design of an appropriate extractor system that provides a sound practical and theoretical basis for a flowsheet is a further requirement. In this study, we investigated effective separation by solvent extraction using a liquid-liquid counter-current centrifugal contactor that induces a series of Taylor vortices inside a narrow region with a high aspect ratio. The contactor consists of an inner rotor and static outer wall and facilitates extraction with multiple theoretical stages due to countercurrent contact between the organic and aqueous phases. To evaluate extraction performance, the oil-water dispersion, extraction/separation behavior, and mechanism of multi-staging were investigated. The flows inside the contactor were observed and measured by the ultrasonic velocity profiler method and the results were verified by numerical simulation of a single-phase flow [1]. A fine dispersion inside the contactor was simulated by altering the volume of the fluid model in the multiphase flow simulation, and the effects of the wetting properties of the inner rotor and interfacial tension were highlighted [2]. Continuous extraction experiments have been performed to study the effects of operating conditions (e.g., axial flow rates and rotation speed) and extraction systems with fast and slow extraction kinetics (e.g., Zn(II) extraction by di(2-ethylhexyl) phosphoric acid (D2EHPA) and Cs(I) extraction by calix[4]arene-bis(*t*-octylbenzo-crown-6) (BOBCalixC6)) in the presence of certain additives [1,3]. Multi-staging was readily accomplished by D2EHPA-Zn(II) due to its fast kinetics, whereas multi-staging was difficult for BOBCalixC6-Cs due to slow extraction kinetics. However, using a more lipophilic inner rotor resulted in a finer dispersion and some multi-staging was observed. Surface-activating agents, such as sodium di(2-ethylhexyl) sulfosuccinate and sodium dodecyl sulfate, and a surface-protective agent, polyethylene glycol, have also been used in Taylor-Couette (TC) flows under appropriate conditions for phase separation [4]. The effect of synergistic agents on lanthanide extraction have also been studied for *N*,*N*,*N′*,*N′*-tetraoctyl diglycolamide (slow extraction kinetics) in the presence of a water-soluble masking agent and synergist (such as *N*,*N*,*N’*,*N’*-tetraethyl-3,6-dioxaoctane-1,8-diamide and nonanoic acid) [5]. Interestingly, such chemicals worked more effectively in TC flows compared with batch extraction. A back extraction has also been performed and the acid concentration needed for the back extraction was greatly minimized [6]. These results suggest that fast extraction kinetics are needed for effective multi-staging in TC flows. Therefore, the effect of extraction rate on separation performance in TC flows was studied for Sm(III)/Eu(III) separation by comparing the distribution ratio (*D*) and the separation factor (*SF*; ratio of distribution ratios, *D*) under equilibrium and non-equilibrium conditions [7]. For separating Sm(III) and Eu(III) by D2EHPA, the extraction rates of Sm and Eu were similar because they are adjacent trivalent lanthanides. For non-equilibrium conditions, the ratio of the gradient of *D* with respect to time, $SF_{\mathrm{Eu/Sm,non\text{-}eq.}} = (\mathrm{d}D_{\mathrm{Eu}}/\mathrm{d}t)/(\mathrm{d}D_{\mathrm{Sm}}/\mathrm{d}t)$, was $SF_{\mathrm{Eu/Sm,non\text{-}eq.}} < SF_{\mathrm{Eu/Sm,eq}}$. Correspondingly, the number of theoretical stages for Sm estimated for extraction at equilibrium was lower than that of Eu, that is, $SF_{\mathrm{Eu/Sm,TC.}} < SF_{\mathrm{Eu/Sm,eq}}$, where $SF_{\mathrm{Eu/Sm,TC}}$ indicates the SF in case of continuous extraction operation with TC flow. If extraction is based on equilibrium conditions, the number of theoretical stages for each metal ion should be the same. In the case of separations with a large difference in extraction kinetics resulting in a large difference in the SF values, that is, $SF_{\mathrm{non\text{-}eq.}} > SF_{\mathrm{eq}}$, it is expected that separations not governed by the extraction equilibrium may be possible. Under such circumstances, the separation of Fe(III)/Y(III) by D2EHPA has been re-examined. The D2EHPA can extract Fe(III) effectively but the extraction has slow kinetics [8, 9]. Thus, for the Fe(III)/Y(III) system, we compared the extraction kinetics for conventional liquid-liquid extraction performed under equilibrium conditions and continuous extraction with a TC flow.

2. Experimental

2.1 Centrifugal Contactor

A schematic of the centrifugal contactor is given in Figure 2 [7]. When the rotation speed of the inner rotor reaches a critical point, a series of Taylor vortices are induced [10]. The TC flow in this study has a flow region with a high aspect ratio and the rotation speed is high enough to produce stable turbulent Taylor vortices [11]. The dispersed organic phase from the bottom inlet ascends through a series of Taylor vortices and comes into contact with the continuous aqueous phase, which originates from the inlet at the top. The lighter organic solvent (*n*-dodecane) ascends the column because of the difference in specific gravity and overflows from the top outlet. The heavier aqueous phase is pumped out from the bottom outlet. Phase separation was achieved in the settling zones (intact tube covering the inner rotor, 20 mm in height) at the top and bottom of the contactor.

Table 1. Dimensions of the contactor.

Variable	Symbol	Value	Unit
Radius of inner rotor	D_i	15	mm
Radius of outer wall	D_o	20	mm
Width of fluid region	D_o-D_i	5	mm
Height of fluid region	H_f	200	mm
Radius ratio	D_i/D_o	0.75	-
Aspect Ratio	H_f/d	40	-
Hight of upper settling part	H_u	30	mm
Diameter of inlet hole for aqueous phase	D_a-inlet	3	mm
Diameter of outlet hole for aqueous phase	D_a-outlet	3	mm
Diameter of inlet hole for organic phase	D_o-inlet	3	mm
Diameter of outlet hole for organic Phase	D_o-outlet	3	mm

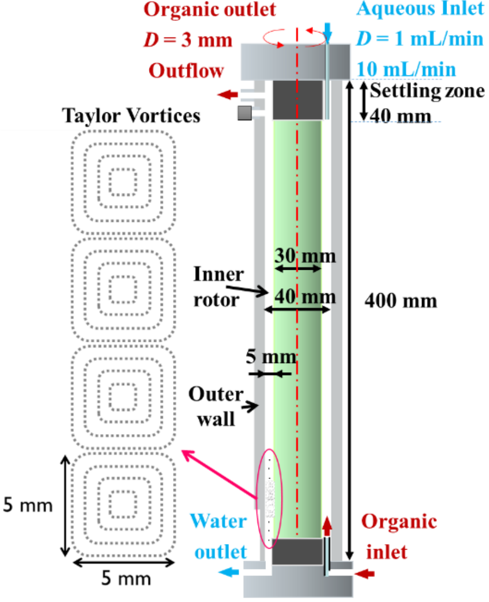

Figure 2. Schematic of contactor

2.2 Solutions and experimental conditions

The experimental conditions for batch extraction and continuous extraction with TC flow are listed in Tables 2 and 3, respectively. The change in the metal ion (Fe(III) and Y(III)) distribution over time was used to assess performance. To compare separation performance in batch extraction and continuous extraction with TC flow, solutions containing various Fe(III) concentrations and a fixed Y(III) concentration were tested. The Fe(III) and Y(III) concentrations in the aqueous phase were measured by inductively coupled plasma atomic emission spectrometry (ICPE-9000, Shimadzu). Several approaches have been described for measuring extraction kinetics, including the batch method [12], the single droplet method [13], stopped-flow apparatus [9], the constant area cell approach [8,14,15], and using specialized equipment [16]. In this study, the batch method was used.

Table 2. Experimental conditions for batch extraction tests.

		value	unit
Operation	Temperature	25	°C
	time	30 - 350000	s
Aqueous phase	volume	3	ml
	Y(III), Fe(III)(single)	5	mmol/L
	HNO_3	0.01	mol/L
	Ionic strength($NaNO_3$)	0.2	mol/L
Organic phase	Volume	3	ml
	Diluent	*n*-dodecane	
	D2EHPA	0.01	mol/L

Table 3. Experimental conditions for continuous extraction tests with TC.

		value	unit
Operation	Ttemperature	25	°C
	Time	60	min
	Rotation speed	1400	rpm
Aqueous phase	flow rate	10	ml/min
	Y(III)	0.5	mmol/L
	Fe(III)	0.3 - 5	mmol/L
	HNO_3	0.01	mol/L
	Ionic strength($NaNO_3$)	0.2	mol/L
Organic phase	Flow rate	3	ml
	Diluent	*n*-dodecane	
	D2EHPA	0.01	mol/L

The extraction equilibrium of trivalent metal ions ($M^{3+} = Fe^{3+}$, Y^{3+}) with D2EHPA is described as equation (1), where HR and $(HR)_2$ indicate monomeric and dimeric formation of D2EHPA because D2EHPA exists in dimer form in a long-chain hydrocarbon, such as *n*-dodecane. The species with bar and non-bar indicate the species exist in organic phase and aqueous phase, respectively.

$$M^{3+} + 3\overline{(HR)_2} \rightleftarrows \overline{MR_3(HR)_3} + 3H^+ \tag{1}$$

The distribution ratio is defined as the ratio of metal ion concentrations in the organic ($C_{\mathrm{org.eq}}$) and aqueous ($C_{\mathrm{aq,eq}}$) phases at equilibrium, $D = C_{\mathrm{org.eq}}/C_{\mathrm{aq,eq}}$. In the D2EHPA system, the extraction equation is given by equation (2),

$$K_{ex} = \frac{\left[\overline{MR_3(HR)_3}\right]\left[H^+\right]^3}{\left[M^{3+}\right]\left[\overline{(HR)_2}\right]^{*3}} = D\frac{\left[H^+\right]^3}{\left[\overline{(HR)_2}\right]^{*3}} \tag{2}$$

where the bars indicate "in the organic phase" and $[(HR)_2]^*$ denotes the effective molar concentration of $(HR)_2$ calculated by Alstad's equation [17]. The extraction at equilibrium is described by equation (3),

$$\left[\overline{(HR)_2}\right]^* = \gamma^*\left[\overline{(HR)_2}\right] \quad , \quad \log\gamma^* = -A\left[\overline{(HR)_2}\right]^{1/2} \tag{3}$$

where $A = 0.83$ for *n*-dodecane [18], and the effective concentration of the D2EHPA dimer is used as shown in equation (4).

$$\log D + 3\log[H^+] = 3\log\left[\overline{(HR)_2}\right]^* + \log K_{ex} \tag{4}$$

Equation (4) is derived from equations (2) and (3), and the *log-log* plot gives the extraction coefficient, K_{ex}.

3. Results and Discussion

3.1 Extraction in equilibrium state

Figure 4 shows the results of the slope analysis by the least squares method for a fixed gradient of 3. In the equilibrium state, Fe(III) was more readily extracted than Y(III), namely, $D_{Y(III),eq} < D_{Fe(III),eq}$ was confirmed. The kinetics of the extraction, where there is a contact time dependency for $D_{Y(III)}$ and $D_{Fe(III)}$, by D2EHPA, are shown in Figure 5. Before the extraction reached equilibrium, the order was $D_{Y(III)} > D_{Fe(III)}$. Fe(III) has slow extraction kinetics, but at equilibrium was more readily extractable than Y(III) by D2EHPA. The slope analysis confirmed that the stoichiometries of Y(III)- and Fe(III)-D2EHPA were the same, which implies that the extraction mechanisms for the two metal ions were the same; hence, the difference in extractabilities was attributed to the slow exchange reaction of hydrated water molecules. The rate-determining step for D2EHPA extraction of Fe(III) and Y(III) may be the complexation step at the oil-water interface where the intermediate, MR_2^+ (M: metal ion, R: D2EHPA), is transferred to the organic phase [19-21].

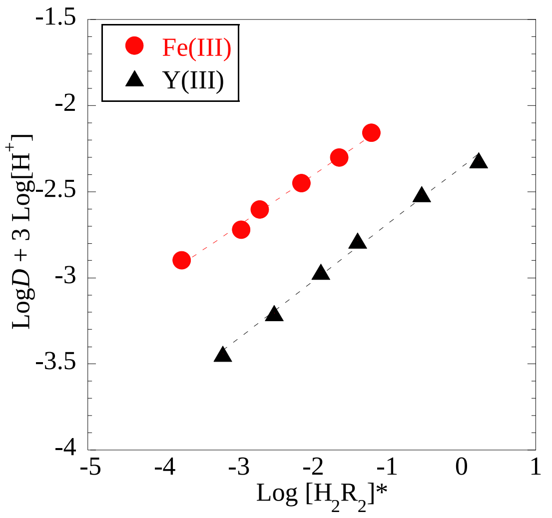

Figure 4. Slope analysis for Y(III)/Fe(III)-D2EHPA extraction systems in nitric acid

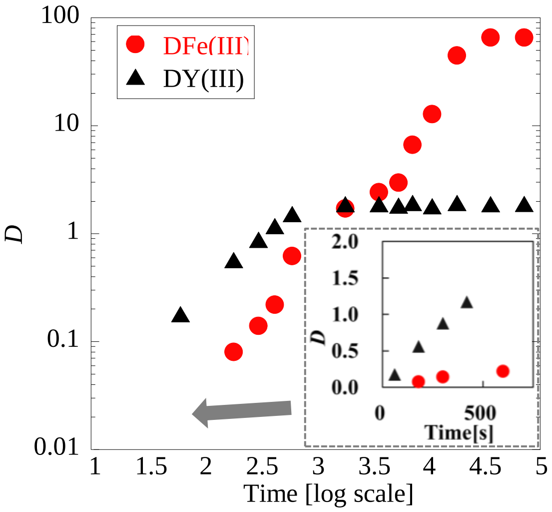

Figure 5. Contact time dependency of $D_{Fe(III)}$ and $D_{Y(III)}$.

3.2 Comparison of batch extraction and continuous extraction by the centrifugal contactor

Figure 6 compares $D_{Y(III)}$, $D_{Fe(III)}$, and $SF_{Y(III)/Fe(III)}$ for (a) batch extraction and (b) continuous extraction with TC flow. In the case of batch extraction, $D_{Y(III),eq} < D_{Fe(III),eq}$ was obtained, and $SF_{Y(III)/Fe(III),eq}$ was less than 1, namely, Y(III) cannot be concentrated from the mixture of Y(III) and Fe(III) using conventional batch extraction. For continuous extraction with TC flow, the order of D was reversed compared with batch extraction, that is, $D_{Y(III),TC} > D_{Fe(III),TC}$, so that $D_{Fe(III)}$ was lower and $D_{Y(III)}$ was higher for the TC extraction experiment. This reversal of order of D term resulted in $SF_{Y(III)/Fe(III),TC}$ being much greater than 1, indicating that Y(III) can be effectively separated from a mixture of Y(III) and Fe(III) based on the extraction kinetics. Furthermore, when the metal/ligand ratio and ratio were high, namely, when extraction of Y(III) and Fe(III) was more competitive, $SF_{Y(III)/Fe(III)}$ was high. This effect is also attributed to the difference in the extraction kinetics of Y(III) and Fe(III) by D2EHPA as a

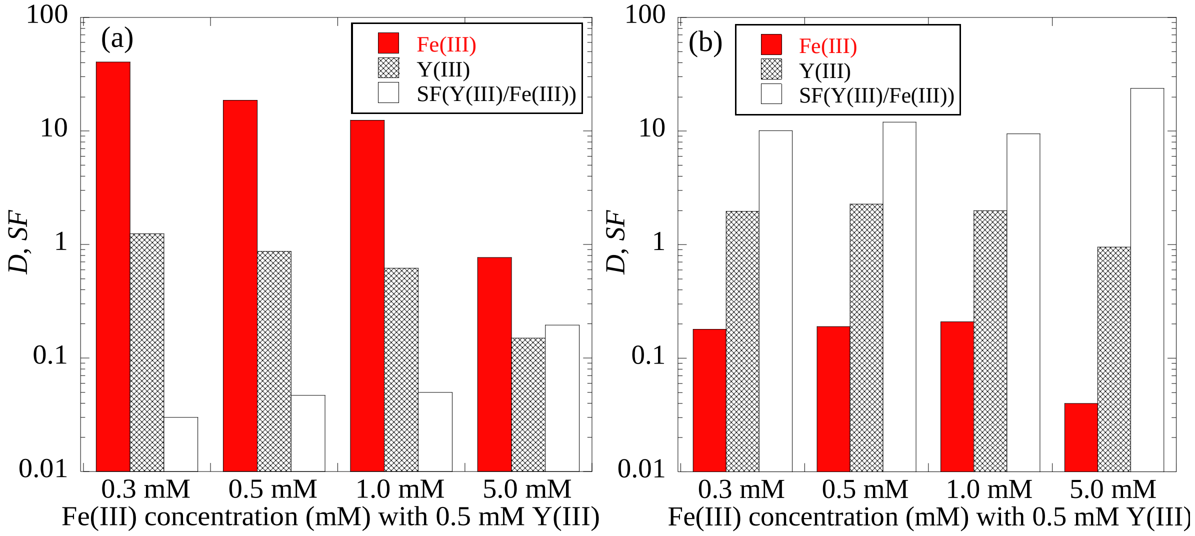

Figure 6. Comparison of D and SF for Fe(III) and Y(III) during (a) batch extraction (equilibrium) and (b) continuous extraction with TC flow (non-equilibrium).

result of high mass transfer due to the countercurrent contact of both phases in a TC flow. Thus, by combining forward and back extractions in a TC flow, much more effective separation can be achieved.

4. Conclusion

A unique separation using a liquid-liquid countercurrent centrifugal contactor was demonstrated by comparing the performance for continuous and batch extractions of Fe(III) and Y(III) by D2EHPA. Separation with countercurrent TC flow was governed by the extraction equilibrium and by the difference in extraction kinetics between the equilibrium and non-equilibrium states. In the batch extraction experiment, Fe(III) was more readily extracted than Y(III) ($D_{Y(III),eq} < D_{Fe(III),eq}$), but for non-equilibrium conditions, Y(III) was more readily extracted than Fe(III) ($D_{Y(III),non\text{-}eq} > D_{Fe(III),non\text{-}eq}$). For continuous extraction with a TC flow, Y(III) was more readily extracted than Fe(III) ($D_{Y(III),TC} > D_{Fe(III),TC}$), For conditions with higher metal/ligand and Y(III)/Fe(III) ratios in the case of continuous extraction with a TC flow, $SF_{\mathrm{Y(III)/Fe(III)}}$ was slightly increased. There have been few studies of the differences in extraction kinetics. Further research on extraction kinetics, including the effect of synergistic agents, the effect of masking agents on extraction performance in a TC flow, and relationships between extraction kinetics and separation performance, will provide new extraction/separation methods.

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