

Solvent extraction of Terbium(III) from chloride solution using organophosphorus extractant, its mixture and ionic liquid in the presence of organic acids

Thanh Tuan Tran ¹, Si Jeong Song ², Chang Geun Oh ², Man Seung Lee ²

¹ Faculty of Biological, Chemical and Food Technology, Can Tho University of Technology, Can Tho City 900000, Vietnam

² Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Republic of Korea

Corresponding author: mslee@mokpo.ac.kr (Man Seung Lee)

Abstract: Addition of organic acids to dilute hydrochloric acid solution can improve the extraction of rare earth elements by single cationic extractants. However, the correlation between the chemical structure of organic acids and the extraction of REEs as well as the variation in equilibrium pH has not been elucidated. In this study, we investigated the extraction of Tb(III) from dilute HCl solutions containing an organic acid like formic, lactic, fumaric, or maleic acid. As extractants, single Cyanex 272, a mixture of Cyanex 272 and Alamine 336 (Ala336-Cy272), and an ionic liquid (ALi-Cy272) synthesized by Cyanex 272 and Aliquat 336 were used. The speciation of Tb(III) in dilute HCl solutions containing organic acids was analyzed. In extraction of Tb(III), organic acids showed two roles as complexing and buffering agent, which depended on the chemical structure of the acids. There was some difference in the extraction of Tb(III) between single Cyanex 272 and ionic liquid, ALi-Cy272. During extraction with ALi-Cy272, formic and lactic acid negatively affected the extraction of Tb(III). The fact that the chemical structure of organic acids affected the extraction of Tb(III) from dilute HCl solution by the studied extractants can provide important information on the selection of suitable extraction systems.

Keywords: extraction, Terbium(III), organic acid, ionic liquid, buffer effect

1. Introduction

Rare earth elements (REEs) are used in the manufacture of advanced materials such as permanent magnets, phosphors, catalysts, and biosensors. Moreover, the utilization of REEs has been increasing in hybrid cars and wind power generation (Jung et al., 2018). To meet the increased demand for REEs in the manufacture of advanced materials, the recovery of REEs with high purity from secondary resources is required. Just like other REEs, the recovery of terbium from waste resources like fluorescent lamps and solid oxide fuel cells (SOFCs) has also attracted much interest in recent years due to its wide usage in high-tech industries (e.g sensors, fluorescence, biological indicators, etc.) (Chen et al. 2019; Pavon et al., 2021).

Since the chemical properties of REEs are very similar to each other, solvent extraction has been used in the separation of REEs from the leaching solutions of diverse resources (Truong et al., 2017; Liu et al., 2015; Banda et al., 2013). In the case of separating rare earth metal ions from dilute hydrochloric acid, cationic extractants like D2EHPA, PC88A, and Cyanex 272 are generally used. In general, these extractants extract metal ions through cationic exchange mechanism, which can liberate hydrogen ions from the organic phase to aqueous phase during the extraction, resulting in a decrease in the equilibrium pH of the aqueous phase (Lee and Son, 2017). As the acidity of the aqueous phase increases, the extraction of REEs decreases. In order to alleviate the pH decrease of aqueous phase, some work has been done on the use of saponified extractants and a mixture of cationic extractants and amines. However, use of saponified extractants can cause some environmental problems like the liberation of

NH_4^+ , Ca^{2+} , and Na^+ (Lee et al., 2005a; Lee et al., 2005b). Therefore, it is necessary to find other methods to replace the use of saponified extractants.

Some studies show that the presence of organic acids in hydrochloric acid solution improves the separation factor and extraction percentage of REEs (Yin et al., 2013; Kashi et al., 2018; Satpathy and Mishra, 2017). Besides, the use of ionic liquids synthesized from commercial organophosphorous extractants and tertiary/quaternary amine also increase the extraction of REEs (Raju et al., 2011; Oh et al., 2019; Liu et al., 2014). In general, the formation constants of the complexes between chloride and rare earth ions in dilute HCl solutions is small. The anions of organic acids are in general stronger bases than chloride ion and thus have a strong tendency to form complexes with metal ions. When organic acids are added to the dilute HCl solution containing rare earth ions, the acids can act as a buffer and thus control the solution pH. Most of the work on the effect of organic acid on the separation of REEs has been done by using single organophosphorous acidic extractants. Meanwhile, few results have been reported on the effect of organic acids on the extraction of REEs from the dilute HCl solutions by either a mixture of organophosphorous extractants and tertiary amines or their ionic liquids with quaternary amines.

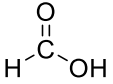
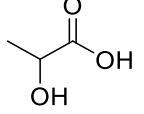
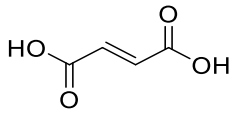
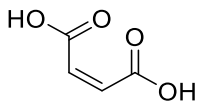
In this work, Cyanex 272, an organophosphorous acid and its mixture with Alamine 336 and an ionic liquid prepared from Cyanex 272 and Aliquat 336 were used for the extraction of Tb(III) from the dilute HCl solution in the presence of mono- and di- carboxyl groups of acids. The effect of the initial pH, the concentration of the extractants and organic acids on the extraction efficiency of Tb(III) was investigated.

2. Materials and methods

2.1. Materials

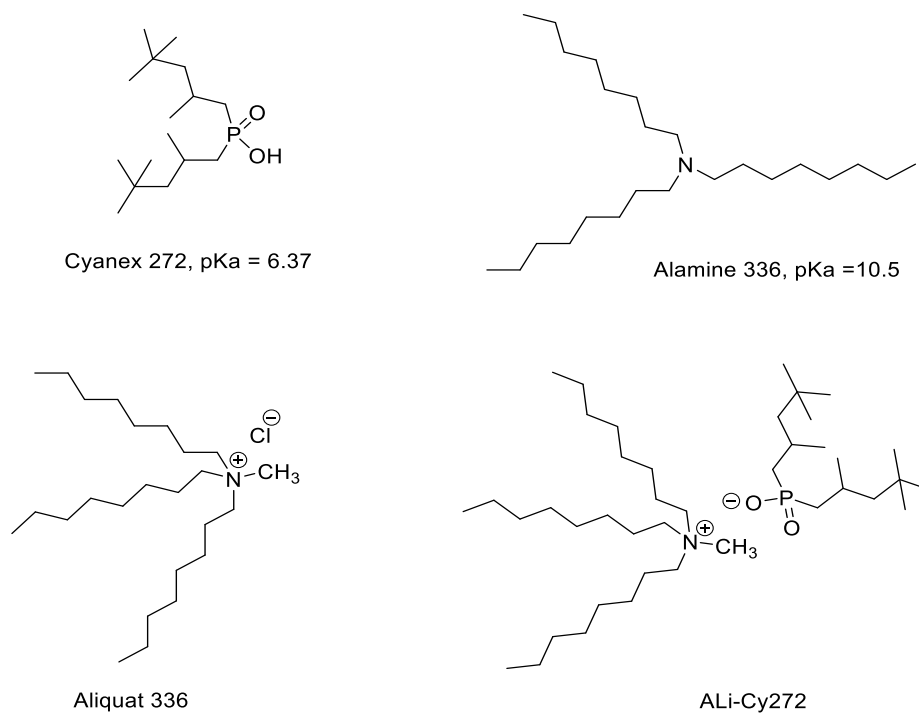
The solutions of terbium(III) chloride were prepared by dissolving a certain amount of TbCl_3 (Alfa Aesar, 99.9%) in doubly distilled water. The pH value of the Tb(III) solution was adjusted by using concentrated hydrochloric acid (HCl, Daejung Chemicals & Metals Co. Ltd., 35%). The concentration of Tb(III) ions in the aqueous solutions was fixed at 100 mg/L in all the experiments. Organic acids such as formic acid (CH_2O_2 , Daejung Chemicals & Metals Co. Ltd., 99%), lactic acid ($\text{C}_3\text{H}_6\text{O}_3$, Daejung Chemicals & Metals Co. Ltd., 90%), fumaric acid ($\text{C}_4\text{H}_4\text{O}_4$, Daejung Chemicals & Metals Co. Ltd., 99%), and maleic acid ($\text{C}_4\text{H}_4\text{O}_4$, Daejung Chemicals & Metals Co. Ltd., 99%) were used without any treatment. The chemical structures and pK_a values of these acids are shown in Table 1.

Table 1. Properties and chemical structures of organic acids at 25°C

Organic acids	Chemical formula	Solubility in water, g/L	Acidity (pKa)	Structure
Formic acid (Methanoic acid)	CH_2O_2	Miscible	3.744	
Lactic acid (2-Hydroxypropanoic acid)	$\text{C}_3\text{H}_6\text{O}_3$	Miscible	3.85, 15.1	
Fumaric acid (<i>cis</i> -Butenedioic acid)	$\text{C}_4\text{H}_4\text{O}_4$	6.3	3.03, 4.44	
Maleic acid (<i>trans</i> -Butenedioic acid)	$\text{C}_4\text{H}_4\text{O}_4$	780	1.97, 6.07	

Commercial extractants such as Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, Cytec Inc., 85%), Alamine 336 (trioctyl amine, BASF Co., 95%), and Aliquat 336 (*N*-methyl-*N,N*-dioctyloctan-1-aminium chloride, BASF Co., 93%) were used without any purification. Commercial grade kerosene (Daejung Chemicals & Metals Co. Ltd., >90%) was used as a diluent. A binary mixture, Ala336-Cy272

was prepared by mixing Cyanex 272 and Alamine 336 at an equimolar concentration ratio in kerosene. An ionic liquid, ALi-Cy272 (*N*-methyl-*N,N*-dioctyloctan-1-aminium bis(2,4,4-trimethylpentyl)-phosphinate) was synthesized by reacting Aliquat 336 and Cyanex 272 according to the method reported in the literature (Fortuny et al., 2012). The synthesis of the ionic liquid, ALi-Cy272 was verified by identifying its chemical structure with FT-IR spectroscopy in our previous work (Tran and Lee, 2020). Organic phases were prepared by diluting the extractants in kerosene to the desired concentrations. The chemical structures of the extractants are presented in Scheme 1.



Scheme 1. Chemical structures of the extractants used in this work

2.2. Methods

Extraction experiments were performed by mixing equal volume of aqueous and organic phase (each 20 mL) in a screwed cap bottle for 30 min using a Burrell wrist action shaker (model 75, USA) at ambient temperature (22 ± 1 °C). The shaken solutions were allowed to stand in a glass separatory funnel for the separation of the two phases. Orion Star thermal scientific pH meter (model A221, USA) was used for the measurement of the pH of the aqueous phase. The concentration of Tb(III) in the aqueous phase before and after the extraction was determined by UV-VIS (Shimadzu UV-vis model 1800) at wavelength of 569 nm.

Extraction percentage (%E) of Tb(III) was calculated from the mass of Tb(III) in the aqueous phase before extraction, m_{initial} and that after extraction, m_{aq} :

$$\%E = \frac{(m_{\text{initial}} - m_{\text{aq}}) \times 100\%}{m_{\text{initial}}} \quad (1)$$

It was assumed that there was no change in the volume of the aqueous and organic phases after the extraction. Replicate experiments were done and the errors in the measured values were within $\pm 5\%$.

3. Results and discussion

3.1. Chemical speciation of Tb(III) in HCl solutions containing organic acids

Since the oxidation state of Tb(III) is +3, Tb(III) can form complexes with chloride ion. However, the stability constants of the complexes between Tb(III) and chloride ion have not been reported. Although the radius of Tb(III) is smaller than that of Gd(III) which is adjacent to Tb(III) in the periodic table, the stability constant of GdCl_2^{2+} ($K = 0.7$ at 25°C) (Lee et al., 2005a) was used in calculating the chemical

speciation of Tb(III). When organic acids (H_nA) are added to the weak HCl solution, several reactions such as the dissociation of organic acids and the complex formation of Tb(III) with the anions of the organic acids can occur. In this case, the dissociation of organic acids depends on the concentration of HCl.

Table 2. Stability constants of the complexes between Tb(III) and lactate ions ($I= 2.0$ at 25°C) (Nilsson and Nash, 2007)

Reactions	Overall stability constants
$\text{Tb}^{3+} + \text{C}_3\text{H}_5\text{O}_3^- = [\text{Tb}(\text{C}_3\text{H}_5\text{O}_3)]^{2+}$	$\beta_1 = 4.03 \times 10^2$
$\text{Tb}^{3+} + 2\text{C}_3\text{H}_5\text{O}_3^- = [\text{Tb}(\text{C}_3\text{H}_5\text{O}_3)_2]^+$	$\beta_2 = 5.28 \times 10^4$
$\text{Tb}^{3+} + 3\text{C}_3\text{H}_5\text{O}_3^- = [\text{Tb}(\text{C}_3\text{H}_5\text{O}_3)_3]$	$\beta_3 = 1.00 \times 10^6$

Table 2 shows the complex formation constants between Tb(III) and lactate anions such as $[\text{Tb}(\text{C}_3\text{H}_5\text{O}_3)]^{2+}$, $[\text{Tb}(\text{C}_3\text{H}_5\text{O}_3)_2]^+$, and $[\text{Tb}(\text{C}_3\text{H}_5\text{O}_3)_3]$. In order to simplify the calculation of chemical speciation, it is assumed that organic acids act as a monoacid (HA) in the HCl solution. Since pH values of the HCl solution was less than 5, the concentration of hydroxide ions would be very low and thus the formation of Tb(III) hydroxide was not considered. Therefore, the formation of complexes between Tb(III) and chloride/organic anions could be written as follows:



By considering the above reactions, the mass balance of Tb(III) can be expressed as

$$[\text{TbCl}_3]_{\text{total}} = [\text{Tb}^{3+}] + [\text{TbCl}^{2+}] + [\text{TbA}^{2+}] + [\text{TbA}_2^{+}] + [\text{TbA}_3] \quad (7)$$

$$[\text{Cl}]_{\text{total}} = [\text{HCl}]_{\text{total}} + 3[\text{TbCl}_3]_{\text{total}} = [\text{Cl}^{-}] + [\text{TbCl}^{2+}] \quad (8)$$

$$[\text{A}]_{\text{total}} = [\text{HA}]_{\text{total}} = [\text{HA}] + [\text{A}^{-}] + [\text{TbA}^{2+}] + 2[\text{TbA}_2^{+}] + 3[\text{TbA}_3] \quad (9)$$

Since the aqueous solution must satisfy charge balance, the following charge balance equation can be obtained.

$$[\text{H}^{+}] + 3[\text{Tb}^{3+}] + 2[\text{TbCl}^{2+}] + 2[\text{TbA}^{2+}] + [\text{TbA}_2^{+}] = [\text{Cl}^{-}] + [\text{OH}^{-}] + [\text{A}^{-}] \quad (10)$$

Substituting the mass balance equation into the charge balance equation and ignoring the concentration of hydroxide ions gives the following equation.

$$[\text{H}^{+}] \left(1 + \frac{[\text{A}^{-}]}{K_{\text{HA}}} \right) = [\text{Cl}]_{\text{total}} + [\text{A}]_{\text{total}} - 3[\text{Tb}]_{\text{total}} = [\text{HCl}]_{\text{total}} + [\text{A}]_{\text{total}} \quad (11)$$

By solving Eqs. (7), (8), (9), and (11), the equilibrium concentrations of Tb(III), chloride ion, the anion of organic acid and hydrogen ion can be obtained from the initial concentrations of HCl, TbCl_3 , and HA. Since the first dissociation constants of organic acids such as oxalic, lactic, and fumaric acids are quite close, the effect of concentration of lactic and maleic acids on the equilibrium pH was only considered. In calculating the chemical speciation, the concentrations of Tb(III) and HCl were fixed at 100 mg/L and 0.001 mol/L and the concentration of the organic acids was increased to 1.0 mol/L. In Fig. 1, the pH value of the solution rapidly decreased from 3 to about 1.9 as the concentration of lactic acid was below 0.1 mol/L and then constant with the further increase to 1.0 mol/L. Meanwhile, as the concentration of maleic acid in the HCl solution increased, solution pH decreased from 3 to 0.3 at the same conditions. The decrease in the pH of the solution can be explained by the stronger acidity of maleic acid ($K_{\text{a}1} = 10^{-1.97}$) than that of lactic acid ($K_{\text{a}1} = 10^{-3.85}$). These obtained results indicated that the addition of organic acids in the HCl solution containing Tb(III) notably affected the existences of chemical species due to the decrease in pH and the formation of metal complexes, which can affect the extraction behavior of Tb(III) by extractants. Thus, the effect of some variables such as initial pH and the concentration of organic acids and extractants on the extraction of Tb(III) was studied further.

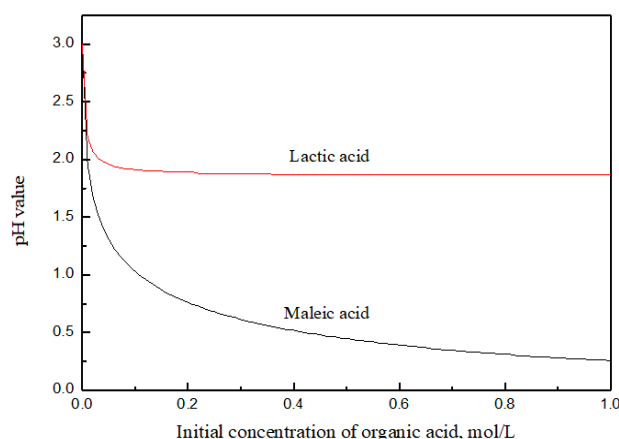
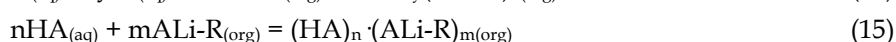
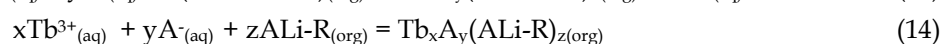
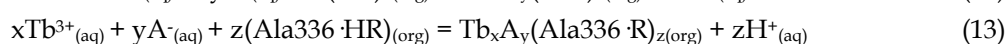
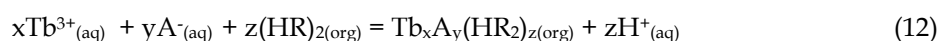


Fig. 1. Effect of the concentration of lactic and maleic acids on the calculated equilibrium pH of the HCl solution at 25°C

3.2. Effect of initial pH on Tb(III) extraction in the presence of organic acids

To investigate the effect of initial pH on the extraction efficiency of Tb(III) from dilute HCl solution by Cyanex 272, Ala336-Cy272, and ALi-Cy272, the initial pH of the solution was varied from 3.0 to 5.0. Concentration of Tb(III) and organic acids in the aqueous phase was fixed at 100 mg/L and 0.1 mol/L, while that of the extractants was 0.003 mol/L. In Fig. 2, the extraction percentage of Tb(III) by Cyanex 272 and Ala336-Cy272 significantly increased from 2.5 to above 79.0% with the increase in initial pH. Tb(III) in the HCl solutions mainly exists as cationic species, which can be extracted by cationic extractants according to ion exchange mechanism. Compared to single Cyanex 272, the addition of Alamine 336 to Cyanex 272 slightly decreased the extraction percentage of Tb(III) due to the interaction of acidic group (-POOH) of Cyanex 272 with the amine group of Alamine 336 (NR₃), which reduces the effective concentration of Cyanex 272 available for the extraction (Satpathy and Mishra, 2017). The presence of lactic acid or maleic acid in the HCl solution facilitated the extraction of Tb(III) as compared to that of formic acid or fumaric acid, which might be attributed to the difference in the formation of Tb(III) complexes with organic anions. In the case of ALi-Cy272, the extraction percentage of Tb(III) was lower than 22.0% from the HCl solution containing formic and lactic acid and the increase in initial pH decreased the extraction percentage of Tb(III). Meanwhile, the extraction percentage of Tb(III) by ALi-Cy272 from fumaric and maleic acid solutions was remarkably increased and was somewhat different from the extraction by single Cyanex 272 or Ala336-Cy272. Since ALi-Cy272 can act as cationic and anionic extractants, the extraction efficiency of Tb(III) by ALi-Cy272 remarkably depends on the existence of ionic species in the aqueous phase (Quinn et al., 2015). Therefore, the competition in the extraction between Tb(III) and formate/lactate anions could be attributed to the low extraction by ALi-Cy272 (Sparekel and Schuur, 2019; Martak and Schlosser, 2007; Oh and Lee, 2018). Besides, the difference in the structure of these organic acids (mono acid and diacids), which is related to the formation of Tb(III) complexes could affect the extraction of Tb(III) by ALi-Cy272. It was noticeable that the extraction of Tb(III) by the extractants from maleic acid solutions was more efficient than from others. The cis-conformation of maleic acid can be the reason for the formation of cyclic complexes with Tb(III), facilitating the extraction of metal complexes to the organic phases. Extraction reactions of Tb(III) by the extractants can be written as:



where HA is organic acid and HR, Ala336, and ALi-R represent Cyanex272, Alamine 336, and ALi-Cy272, respectively.

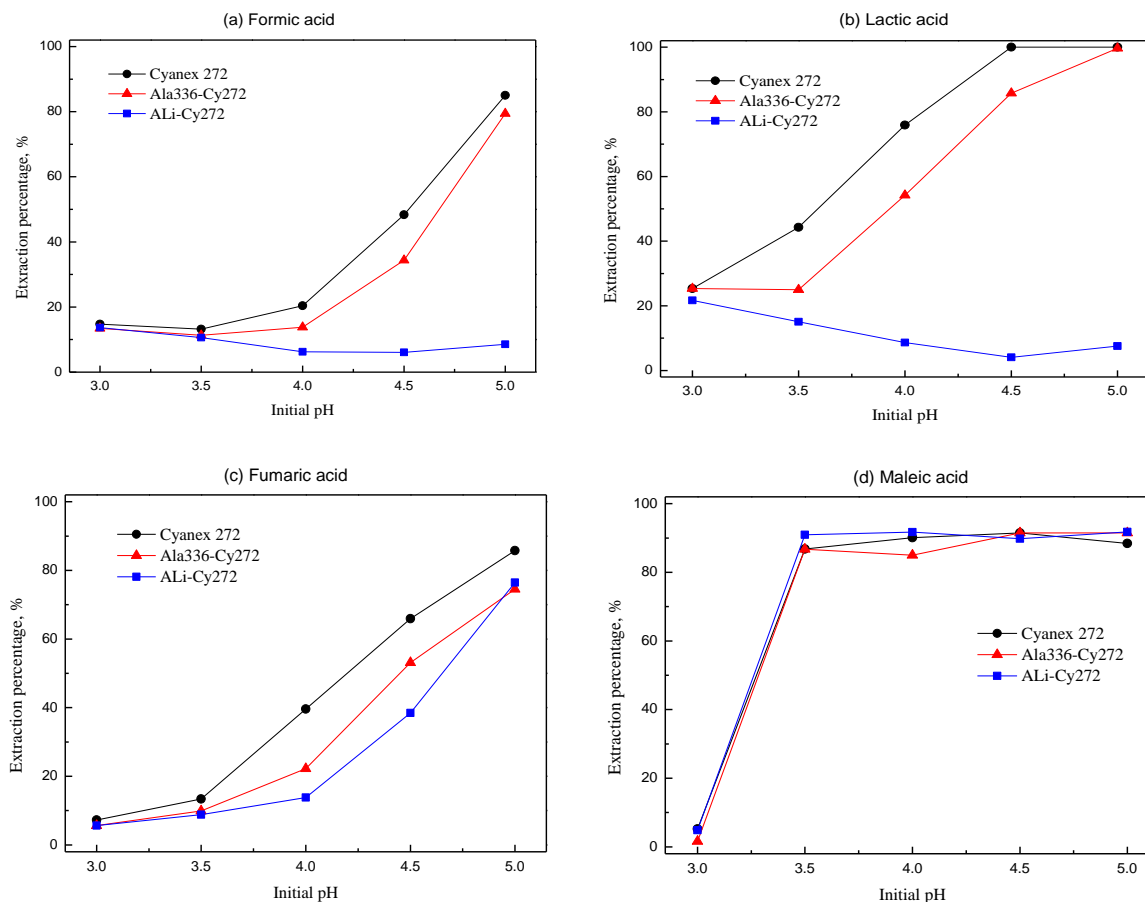


Fig. 2. Effect of initial pH on the extraction of Tb(III) in the presence of organic acids. [Extractants] = 0.003 mol/L, [Tb(III)] = 100 mg/L, [organic acid] = 0.1 mol/L

Thus, the extraction behavior of Tb(III) significantly depends on the initial pH of the aqueous phase and the structure of organic acids added to the solution.

3.3. Effect of extractant concentration on the extraction of Tb(III) in the presence of organic acids

To consider the effect of the concentration of the extractants on the extraction of Tb(III) from the HCl solution with or without the addition of organic acids, the concentration of single Cyanex 272, Ala336-Cy272, and ALi-Cy272 was varied from 0.003 to 0.015 mol/L. The concentration of organic acids and Tb(III) in the HCl solution was fixed at 0.3 mol/L and 100 mg/L, respectively and the initial pH of the solution was kept at 3.0. As presented in Fig. 3, the increase in the concentration of the extractants significantly enhanced the extraction of Tb(III) from the aqueous. When no organic acid was added to the aqueous solution, the extraction percentage of Tb(III) by Cyanex 272 and Ala336-Cy272 reached about 60% in the experimental concentration ranges (see Fig. 3a). However, the extraction percentage was improved to 85% by adding organic acids to the solution (see Fig. 3b-3e). The extraction percentage of Tb(III) in the absence of organic acids by ALi-Cy272 was above 96.0%. However, the extraction of Tb(III) by ALi-Cy272 from the solution containing organic acids depended on the nature of organic acids. Namely, the extraction percentages of Tb(III) from the solutions containing formic and maleic acid were 99% and 85%, respectively, while those from formic and lactic acids were less than 30%. The low extraction percentage of Tb(III) from the solutions containing formic and lactic acids can be attributed to the extraction competition between Tb(III) and hydrogen ions.

On the other hand, the effect of extractant concentration on the correlation between the extraction of Tb(III) and the equilibrium pH was also considered. Fig. 4 shows that the equilibrium pH of the solutions slightly increased with the concentration of the extractants according to the following order: ALi-Cy272 > Ala336-Cy272 > Cy272. These results indicated that the organic acids and its dissociated

anions played a role as a buffer solution, which could maintain the pH of the solution during the extraction. This can be explained by the increase in the extraction of Tb(III) in the presence of organic acids by Cyanex 272 and Ala336-Cy272. However, it is difficult to expect a buffering action during the extraction of Tb(III) by ALi-Cy272 because the extraction of Tb(III) depends on the structure of metal complexes with organic anions. Besides, organic acids can be extracted by ionic liquid and thus the extraction of organic acid results in an increase in the equilibrium pH.

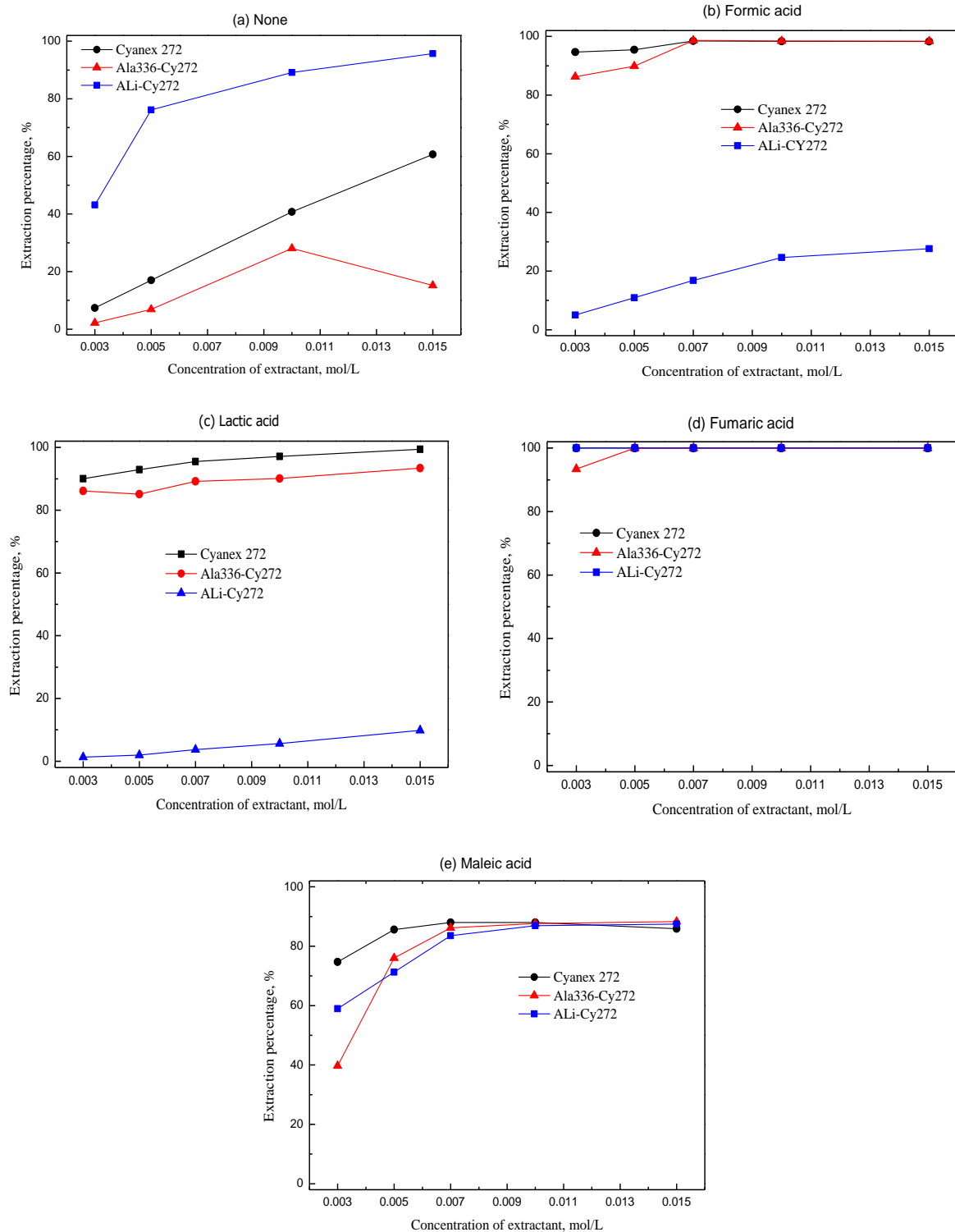


Fig. 3. Effect of the concentration of the extractants on the extraction of Tb(III) without (a) or with ((b)-(e)) the presence of organic acids. Conditions: initial pH = 3, [organic acid] = 0.1 mol/L, [Tb(III)] = 100 mg/L, and [extractant] = 0.003-0.015 mol/L

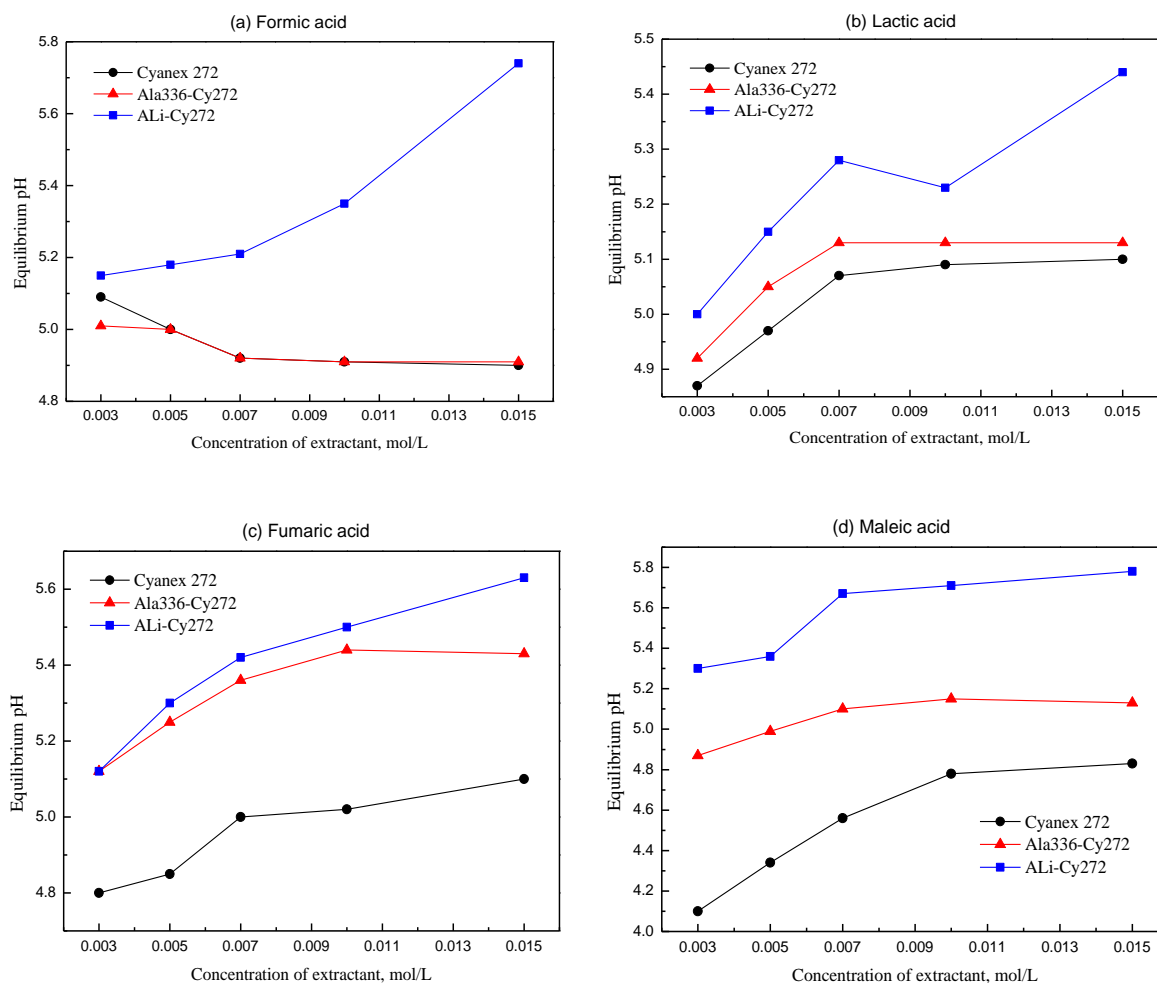


Fig. 4. Variation in the equilibrium pH by single Cyanex 272, Ala336-Cy272, and ALi-Cy272. Conditions: initial pH = 3, [organic acid] = 0.1 mol/L, [Tb(III)] = 100 mg/L, and [extractant] = 0.003-0.015 mol/L.

3.4. Effect of organic acid concentration on the extraction of Tb(III)

The effect of the concentration of organic acids on the extraction of Tb(III) from the HCl solutions was investigated in the range of 0.2 to 0.5 mol/L. The concentration of Tb(III) in the aqueous phase was fixed at 100 mg/L with initial pH 3, while the concentration of the extractants was 0.003 mol/L. In Fig. 5, the increase in the concentration of organic acids slightly raised the extraction percentage of Tb(III) by the three extractants (below 7.0%). The extraction percentage of Tb(III) from the HCl solution containing formic or lactic acids by ALi-Cy272 was decreased, which can be ascribed to the formation of metal complex with formate or lactate anions (Kashi et al., 2018). Unlike lactic acid and formic acid, maleic and fumaric acids are not extracted by ALi-Cy272. Therefore, the effect of adding maleic and fumaric acids on the extraction of metals needs further work.

3.5. Extraction of organic acid from hydrochloric acid solution by ionic liquid

According to the reported literatures, ALi-Cy272, a bi-functional ionic liquid can extract both cationic and anionic species from aqueous solutions (Martak and Schlosser, 2007; Fortuny et al., 2012). Hence, to consider the extraction behavior of organic acids from aqueous solution by ALi-Cy272, a mixture of organic acid and dilute HCl solutions in the absence of Tb(III) was used in this work. The concentration of organic acids in the aqueous solutions was varied from 0.1 to 0.5 mol/L, while the concentration of HCl was maintained at 0.001 mol/L. The initial pH of formic and lactic acid solutions was fixed at 5.0, while that of maleic acid was 7.1 due to its lower solubility in a low pH range. Since the solubility of fumaric acid in water is low, the extraction of fumaric acid was not considered in these experiments.

Extraction experiments were carried out by 0.003 mol/L ALi-Cy272. **Table 3** shows that the equilibrium pH of the solutions was lower than the initial pH, indicating the extraction of organic anions by ionic liquid. The difference between the initial pH and the equilibrium pH was small for maleic acid solutions, while it was noticeable for formic and lactic acid solutions as the concentration of organic acids increased. These results indicated that the buffer effect of the organic acids was less pronounced when their concentration was low. It is difficult to expect the occurrence of buffering action when solution pH is higher than 5 in the case of lactic acid and formic acid with pK_a of 3.86 and 3.75. However, maleic acid whose successive dissociation pK_a values are 1.97 and 6.07 can maintain buffering action within wide range of pH. Therefore, to expect a buffering effect, it is important to adjust the pH according to the pK_a value of the added organic acid.

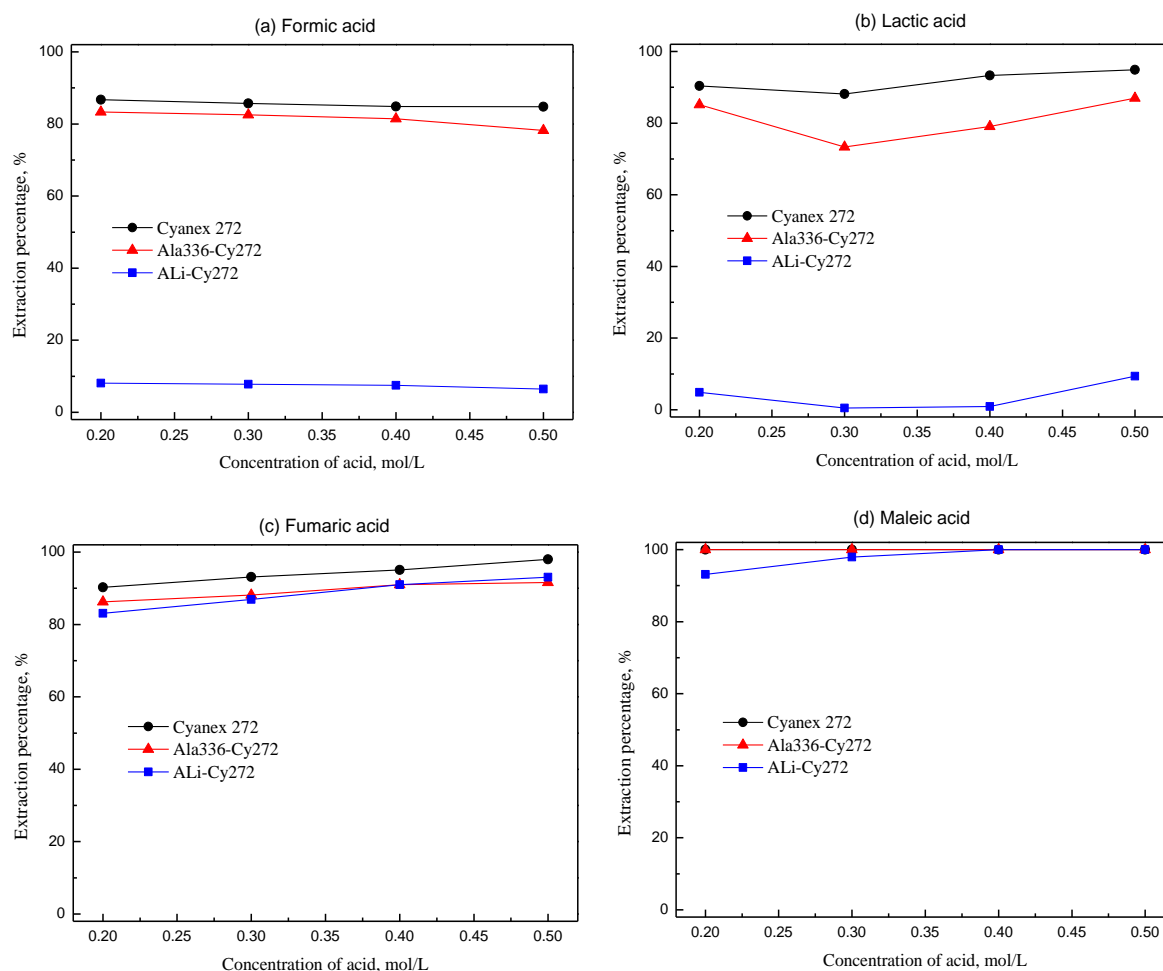


Fig. 5. Effect of the concentration of organic acids on extraction of Tb(III). Initial pH = 3, [Extractants] = 0.003 mol/L, [Tb(III)] = 100 mg/L

Table 3. Equilibrium pH of the HCl solutions after extraction of organic acids by ionic liquid

Organic acid, mol/L	Initial pH_{formic}	Eq. pH_{formic}	$\Delta pH_{\text{formic}}$	Initial pH_{lactic}	Eq. pH_{lactic}	$\Delta pH_{\text{lactic}}$	Initial pH_{maleic}	Eq. pH_{maleic}	$\Delta pH_{\text{maleic}}$
0.1	5	4.69	0.31	5	4.62	0.38	7.1	6.87	0.13
0.2	5	4.65	0.35	5	4.56	0.44	7.1	6.89	0.11
0.3	5	4.61	0.39	5	4.39	0.61	7.1	7.05	0.05
0.4	5	4.58	0.42	5	4.34	0.66	7.1	7.06	0.04
0.5	5	4.57	0.43	5	4.32	0.68	7.1	7.10	0.00

To consider the effect of pH adjustment on the extraction of organic acids by ionic liquid, experiments for the extraction of these organic acids without pH adjustment were tested. Table 4 shows that the initial pH of the acid solutions decreased with the concentration of the acids. The equilibrium pH of the solutions after the extraction was higher than their corresponding initial pH, which can be attributed to the extraction of both hydrogen ions and organic anions by ALi-Cy272 (Oh and Lee, 2018; Oh et al., 2019). It was noticeable that there was less variation in the pH of maleic acid due to its structural characteristics of diacid compared to that of others. The extraction reactions of organic acids by ALi-Cy272 can be written as

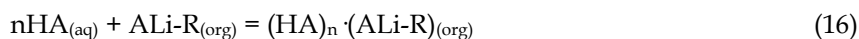


Table 4. Variation in the pH of the HCl solutions without pH adjustment after the extraction of organic acids by ionic liquid

Organic acid, mol/L	Initial pH _{formic}	Eq. pH _{formic}	$\Delta\text{pH}_{\text{formic}}$	Initial pH _{Lactic}	Eq. pH _{Lactic}	$\Delta\text{pH}_{\text{lactic}}$	Initial pH _{maleic}	Eq. pH _{maleic}	$\Delta\text{pH}_{\text{maleic}}$
0.1	2.14	2.81	0.67	2.15	2.81	0.66	1.53	1.70	0.17
0.2	2.18	2.34	0.26	1.88	2.45	0.57	1.25	1.38	0.13
0.3	2.06	2.31	0.25	1.78	2.29	0.51	1.12	1.22	0.10
0.4	1.84	2.08	0.24	1.71	2.19	0.48	1.08	1.12	0.04
0.5	1.81	2.03	0.22	1.66	2.08	0.42	1.06	1.09	0.03

In the metal extraction, bif-functional ionic liquids like ALi-Cy272 can competitively extract metal ions and hydrogen ions from dilute HCl solutions, which increase equilibrium pH of the solution after the extraction. When solution pH is lower than 3, the ionic liquid has stronger affinity for the hydrogen ion than the cationic form of metal ions and thus only hydrogen ions are extracted.

4. Conclusions

The extraction behavior of Tb(III) from dilute HCl solutions containing organic acids like formic, lactic, fumaric, and maleic acid by single Cyanex 272, Ala336-Cy272 and ALi-Cy272 was investigated. The effect of the concentration of organic acids on the equilibrium pH and on the speciation of Tb(III) was analyzed by considering various reactions, mass and charge balance. The increase in the initial pH of the solutions significantly enhanced the extraction efficiency of Tb(III) by Cyanex 272 and its mixture with Alamine 336. However, the extraction of Tb(III) by ionic liquid ALi-Cy272 notably depended on the type of organic acids added. It was found that the extraction percentage of Tb(III) by ALi-Cy272 was slightly reduced for formic and lactic acids, while fumaric and maleic acids showed positive effect on the extraction of Tb(III). Besides, the increase in the concentration of the extractants or organic acids also enhanced the extraction efficiency of Tb(III). The measurement of equilibrium pH after the extraction showed that the presence of organic acids in the HCl solution played a role as buffering system against the change in pH. The extraction of organic acids from the dilute HCl solutions without Tb(III) by the ionic liquid demonstrated that the buffering effect of maleic acid was better than that of formic and lactic acid and the buffering effect was reduced with a decrease in the concentration of organic acids. The addition of organic acids can increase the extraction of Tb(III) from the dilute HCl solutions by the extractants due to the formation of complexes as well as the control of solution pH during the extraction.

Acknowledgments

This work was supported by National Research Foundation of Korea (NRF-2018R1D1A1B07044951).

References

BANDA, R., JEON, H.S., LEE, M.S., 2013. *Extraction behavior of REEs (La, Pr, and Nd) in the presence of EDTA from chloride solutions*. Korean J. Met. Mater. 51, 421-427.

- CHEN, H., SHI, R., OW, H., 2019. *Predicting stability constants for Terbium(III) complexes with dipicolinic acid and 4-substituted dipicolinic acid analogues using density functional theory.* ACS Omega. 4, 20665-20671.
- FORTUNY, A., COLLI, M.T., SASTRE, A.M., 2012. *Use of methyltrioctyl/decylammonium bis 2,4,4-(trimethylpentyl)phosphinate ionic liquid (ALiCy IL) on the boron extraction in chloride medi.* Sep. Purif. Technol. 97, 137-141.
- JUNG, H.B., KIM, S.M., MOON, H.J., OH, Y.S., LEE, Y.J., LEE, H.S., 2018. *Influence of cooling condition of casted strips on magnetic properties of Nd-Fe-B sintered magnets.* Met. Mater. Int. 24, 1422-1431.
- KASHI, E., HABIBPOUR, R., GORZIN, H., MALEKI, A., 2018. *Solvent extraction and separation of light rare earth elements (La, Pr and Nd) in the presence of lactic acid as a complexing agent by Cyanex 272 in kerosene and the effect of citric acid, acetic acid and Titriplex III as auxiliary agents.* J. Rare Earths. 36, 317-323.
- LIU, Y., JEON, H.S., LEE, M.S., 2015. *Separation of Pr and Nd from La in chloride solution by extraction with a mixture of Cyanex 272 and Alamine 336.* Met. Mater. Int. 21, 944-949.
- LEE, M.S., SON, S.H., 2017. *Status and strategy on recycling of domestic used chemical catalysts.* Resour. Recycl. 26, 3-16.
- LEE, M.S., LEE, J.Y., KIM, J.S., 2005a. *Chemical model for the solvent extraction of GdCl₃ from a chloride solution with saponified PC88A.* Met. Mater. Int. 11, 505-511.
- LEE, M.S., LEE, G.S., LEE, J.Y., KIM, S.D.; KIM, J.S., 2005b. *Solvent extraction separation of Nd and Sm from chloride solution with PC88A and saponified PC88A.* Resour. Recycl. 14, 33-42.
- LIU, Y., JEON, H.S., LEE, M.S., 2014. *Solvent extraction of Pr and Nd from chloride solution by the mixtures of Cyanex 272 and amine extractants.* Hydrometallurgy 150, 61-67.
- MARTAK, J., SCHLOSSER, S., 2007. *Extraction of lactic acid by phosphonium ionic liquids.* Sep. Purif. Technol. 57, 483-494.
- NILSSON, M., NASH, K.L., 2007. *Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process.* Solvent Extr. Ion Exch. 25(6), 665-701.
- OH, S.G., SON, S.H., LEE, M.S. *Solvent extraction of Tb(III) from chloride solution using organophosphorous extractant, its mixture and ionic liquids with Amines.* Resour. Recycl. 28, 40-46.
- OH, C.G., LEE, M.S., 2018. *Solvent extraction of Tb(III) from hydrochloric acid solution with Cyanex 272, its mixture and ionic liquid.* Korean J. Met. Mater. 56, 870-877.
- OH, C.G., SON, S.H., LEE, M.S., 2019. *Separation of Tb(III) and Dy(III) from chloride solution by extraction and scrubbing with ionic liquid prepared with Cyanex 272 and Aliquat 336.* Korean J. Met. Mater. 57, 499-505.
- PAVON, S., LAPO, B., FORTUNY, A., SASTRE, A.M., BERTAU, M. 2021. *Recycling of rare earths from fluorescent lamp waste by the integration of solid-state chlorination, leaching and solvent extraction processes.* Sep. Purif. Technol. 272, 118879.
- QUINN, J.E., SOLDENHOFF, K.H., STEVENS, G.W., LENGKEEK, N.A., 2015. *Solvent extraction of rare earth elements using phosphonic/phosphinic acid mixtures.* Hydrometallurgy 157, 298-305.
- RAJU, B., JEON, H.S., LEE, M.S., 2011. *Solvent extraction of Nd from chloride solution with individual and mixed extractants.* Resour. Recycl. 20, 46-51.
- SATPATHY, S., MISHRA, S., 2017. *Extractive separation studies of La(III) and Ni(II) in the presence of lactic acid using DEHPA in petrofin.* Sep. Purif. Technol. 179, 513-522.
- SPAREKEL, L.M.J., SCHUUR, B., 2019. *Solvent developments for liquid-liquid extraction of carboxylic acids in perspective.* Sep. Purif. Technol. 211, 935-957.
- TRAN, T.T., LEE, M.S., 2020. *Interactions Between Ionic Liquid (ALiCY) and TBP and their Use in Hydrometallurgy for Extracting Co(II) and Ni(II).* Korean J. Met. Mater. 58, 423-432.
- TRUONG, H.T., KIM, Y.H., LEE, M.S., 2017. *Separation of rhenium (VII) and vanadium (V) from hydrochloric acid solutions by solvent extraction.* Korean J. Met. Mater. 55, 724-731.
- YIN, S., WU, W., BIAN, X., ZHANG, F., 2013. *Effect of complexing agent lactic acid on the extraction and separation of Pr(III)/Ce(III) with di-(2-ethylhexyl)phosphoric acid.* Hydrometallurgy 131-132, 133-137.