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Comparison of Extraction Ability between a Mixture of Alamine 336/Aliquat 336 and D2EHPA and Ionic Liquid ALi-D2 from Weak Hydrochloric Acid Solution

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Abstract: The development of extraction systems to improve the extraction efficiency of metals using commercial extractants and ionic liquids is of importance. The extraction behavior of Co(II) between mixture of Alamine 336/Aliquat 336 and D2EHPA and synthesized ionic liquid ALi-D2 was compared in this work. Some factors, such as equilibrium pH, properties of the extractants, and concentration of components in the mixture had a remarkable effect on the extraction of Co(II). The interactions occurring in the mixtures as well as the change in solution pH were analyzed. Co(II) was completely extracted by ionic liquid when equilibrium pH was higher than 6.5, while it was difficult to extract Co(II) by employing the mixture of D2EHPA and Alamine 336/Aliquat 336. The formation of ionic liquid in the mixture of D2EHPA and Aliquat 336 was verified through FT-IR spectra. In addition, the competition extraction of hydrogen ion and Co(II) by ionic liquid ALi-D2 was explained. Among the three kinds of extractants, the ionic liquid showed the best extraction efficiency for Co(II) and pH control from weak acidic solutions. The present study provides valuable information on the extraction behavior of metal ion by the mixtures of commercial extractants, and thus can give some light on the development of metal extraction systems.

Keywords: ionic liquid; extraction; D2EHPA; Aliquat 336; Alamine 336; cobalt(II)

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1. Introduction

In hydrometallurgy, solvent extraction is considered to be an efficient method for the separation and recovery of valuable metals from the leaching solution of primary and secondary sources. It is important to select an appropriate extractant system for the target metal ions from diverse leaching solutions. In solvent extraction with mixtures of extractants, the efficiency and selectivity of the extractant mixtures greatly depend on some parameters such as the properties of the constituent extractants, the composition of the mixture, the nature of diluent, and the presence of salts in the aqueous solutions [1–8]. Among these factors, the interactions occurring in the mixtures have a significant effect on the extraction behavior of metal ions by the mixtures [8]. In some mixture of extractants, synergistic effects were observed for the extraction of specific metal ions. For example, adding amines to acidic extractants has some advantages in the extraction of metal ions from weak acidic medium [1,2,6,9]. Namely, a mixture of Alamine 336 (a blend of octyl and decyl tertiary amines) and organophosphorus acids such as Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid), PC88A (2-ethylhexyl-2-ethylhexyl phosphonic acid) and D2EHPA (bis(2-ethylhexyl)phosphoric acid) showed synergistic effect on the extraction for rare earth elements (REE) [9]. The addition of tertiary amines such as Alamine 308/Alamine 336 to organophosphorus acids (Cyanex 272, D2EHPA) showed the great efficiency for the selective extraction of Co(II) or Mn(II) from weak acidic chloride solutions [2,10].

In the solvent extraction by extractant mixtures, the presence of interactions that leads to the formation of some species in the organic phase affects the extraction efficiency [1]. Instead of mixing some extractants, synthesis of some kinds of task specific ionic liquids (ILs) is regarded as a means to achieve synergistic extraction [11,12]. In particular, the synthesized ILs derivated from commercial extractants such as Aliquat 336 (*N*-Methyl-*N*,*N*,*N*-trioctylammonium chloride) or Cyphos IL (phosphonium ionic liquid) have been employed for the extraction and separation of metals [11–18]. Some advantages of the above-mentioned ILs are good extractability, efficient separation, high recovery, and environmental friendliness [14,18]. The dual function of synthesized ILs has also been noted in recent studies because these synthesized ILs not only show good separation of metals but also extraction of hydrogen ions which contribute to control solution pH, resulting in favorable extraction [3,18]. These ILs can extract metal species by either ion exchange or ion pair mechanism [15,19].

According to previous works [20,21], ILs can form when D2EHPA and Aliquat 336 are mixed at a specific composition. However, this prediction was only based on the variation of physical properties of mixture with composition and the shift of characteristic peaks on the spectra such as FT-IR (Fourier-transform infrared spectroscopy), ATR-IR (Attenuated total reflection infrared spectroscopy), and NMR (Nuclear magnetic resonance spectroscopy). Therefore, further investigation on the formation of ILs in binary mixture by comparison on solvent extraction by the mixtures and corresponding ILs is necessary. In this work, the extractant mixtures of D2EHPA and Alamine 336/Aliquat 336 and synthesized IL (ALi-D2) were employed to compare the extraction behavior of Co(II). Besides, the interaction between the components in the extractant mixtures was explored. Co(II) was chosen in this work because it is a rare metal and can be extracted by single D2EHPA from weak acidic solutions. Some factors such as mole fraction of D2EHPA in the mixtures, the concentration of mixtures and IL, and solution pH were investigated. Furthermore, the change in solution pH caused by corresponding components was measured to clarify the extraction behavior. The characteristics of the mixed extractants was also analyzed by FT-IR spectra. From the obtained results, this work provides important information for the selection of adequate binary mixtures and the development of efficient metal extraction systems.

2. Experimental Section

2.1. Reagents and Analysis

The commercial extractants such as Aliquat 336 (BASF Co., Ludwigshafen, Germany, 93%), Alamine 336 (a mixture of tri-octyl/decyl amine, BASF Co., Ludwigshafen, Germany, 95%), D2EHPA (Daihachi Chemicals, Osaka, Japan, 95%) were used without purification. Organic phases were prepared by diluting the extractants with kerosene (Daejung Co., Shiheung, Korea, >90%). Ionic liquid, IL ALi-D2, was synthesized by mixing an equimolar concentration of Aliquat 336 (R_4NCl, BASF Co., Ludwigshafen, Germany, 93%) and D2EHPA (HA) (Daihachi Chemicals, Osaka, Japan, 95%) as reported in the literature [16,18]. A sufficient amount of $NaHCO_3$ (Daejung Co., Shiheung, Korea, 99%) was added to the mixture to promote the formation of IL ALi-D2. The final product, IL ALi-D2, was rinsed multiple times with distilled water. The synthetic reactions could be expressed as

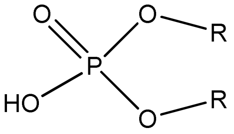
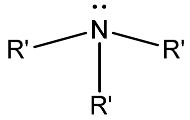
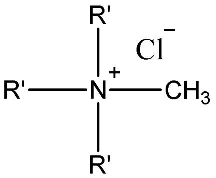
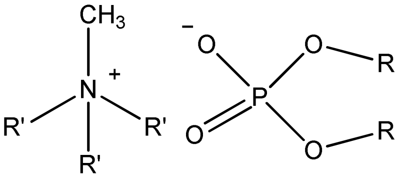
$$R_4NCl + HA \leftrightarrow R_4NCl{\cdot}HA \tag{1}$$

$$R_4NCl{\cdot}HA + NaHCO_3 \leftrightarrow R_4NA + CO_{2(g)} + NaCl + H_2O \tag{2}$$

Binary mixtures of D2EHPA and Alamine 336/Aliquat 336 were prepared in the desired composition range (e.g., mole fraction of D2EHPA was varied from 0.2 to 0.8) at ambient temperature (22 ± 1 °C), and the chemical composition of the mixtures was determined by weight measurements. The chemical structures of these extractants are given in Table 1.

Aqueous solutions containing 500 mg·L^{-1} Co(II) were prepared by dissolving the corresponding amount of $CoCl_2 \cdot 6H_2O$ (Junsei Co., Tokyo, Japan, > 99%) in doubly distilled water. HCl (Dae Jung Chemicals, Shiheung, Korea, 35%) was also added to adjust the pH of the solution. All the employed chemicals were of analytical grade.

Table 1. The name and structure of extractants.

Extractant	Structure
Bis(2-ethylhexyl)phosphoric acid (D2EHPA)	
N,*N*-dioctyl-1-octylamine (Alamine 336)	
N-methyl-*N*,*N*,*N*-trioctylammonium chloride (Aliquat 336)	
N-methyl-*N*,*N*,*N*-trioctylammonium bis(2-ethylhexyl)phosphate (IL ALi-D2)	

note: R and R′ are 2-ethylhexyl and octyl groups, respectively.

2.2. Procedures

The extraction experiments were carried out by shaking an equal volume of aqueous and organic phase (20 mL each) in a screwed cap bottle using a wrist action shaker (Burrell model 75, Pittsburgh, PA, USA) for 30 min. All the extraction experiments were employed at ambient temperature (22 ± 1 °C). After shaking, the two phases were allowed for phase disengagement in a separating funnel. Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany) was used to measure the metal concentration in aqueous phase before and after extraction. The concentration of metals in the organic phase was obtained by mass balance. Solution pH in aqueous phase before and after extraction was measured by a thermal scientific pH meter (Orion Star A211, Thermo Scientific, Waltham, MA, USA) and volumetric titration method.

Based on the concentration of Co(II) in the aqueous phase before extraction $[Co]_i$ and after extraction $[Co]_{aq}$, the extraction percentage (%E) of Co(II) was calculated as: $\%E = \frac{\left([Co]_i - [Co]_{aq}\right) \times 100}{[Co]_i}$. It was assumed in calculating the extraction percentage that there was no change in the volume of the two phases during the extraction. Most of the experiments were replicated and the error associated with the extraction was around ±5%.

3. Results and Discussion

3.1. Comparison of Co(II) Extraction between the Mixtures of D2EHPA and Alamine 336/Aliquat 336 and Ionic Liquid IL ALi-D2

3.1.1. Effect of Equilibrium pH on Co(II) Extraction

The extraction of Co(II) by organophosphorus acids like D2EHPA is proportional to equilibrium pH (pH_{eq}) [22–24]. To investigate the effect of pH on Co(II) extraction by the mixture of D2EHPA and Alamine 336/Aliquat 336 and IL (IL ALi-D2), extraction experiments were performed by varying initial pH of the solution from 1 to 5. After extraction, equilibrium pH was measured and the value of pH_{eq} was displayed in Table 2. In these experiments, the mole fraction of D2EHPA in the mixture was fixed at 0.6 on the basis of the reported literature [5,20]. The concentration of the mixtures and IL was kept at 0.5 M. The concentration of Co(II) was 500 mg·L^{-1} and the volume ratio of the two phases was unity.

Table 2. The results of equilibrium pH after Co(II) extraction by mixture of D2EHPA and Alamine 336/Aliquat 336 and IL.

Initial pH	**pH_{eq}**		
	Alamine 336 + D2EHPA	**Aliquat 336 + D2EHPA**	**IL ALi-D2**
1	1.23	0.67	3.56
2	2.35	0.86	6.52
3	3.34	0.88	7.01
4	3.65	0.95	7.19
5	3.70	0.96	7.25

note: Conditions: [mixture] = [IL] = 0.5 M; mole fraction of D2EHPA in mixture was 0.6; [Co(II)] = 500 mg·L^{-1}; diluent: kerosene; O/A = 1:1.

The results show that the extraction percentage of Co(II) by IL was the highest among the three kinds of extractants. Some difference in extraction behavior was observed in the experimental pH ranges (Figure 1). The difference in Co(II) extraction percentage among the three kinds of extractants was related to the equilibrium pH. Table 2 shows that pH_{eq} values are different in each extractant system. In the case of IL, pH_{eq} quickly increased from 3.56 to 7.25 with the increase in initial pH from 1 to 5 while that was lightly increased from 1.23 to 3.34 and then decreased in mixture of D2EHPA and Alamine 336. In contrast, pH_{eq} values were lower than initial pH ($pH_{eq} < 1$) in the case of mixture of D2EHPA and Aliquat 336.

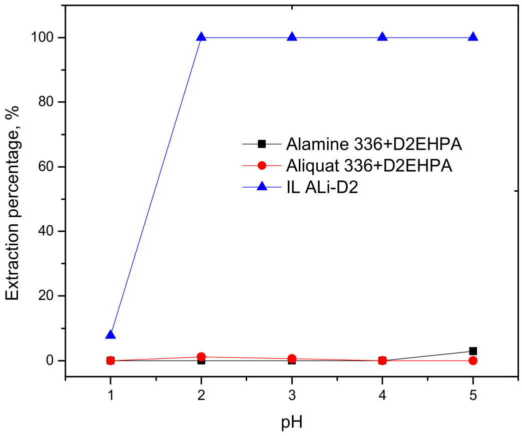


Figure 1. Effect of pH on Co(II) extraction by extractants. Conditions: [mixture] = [IL] = 0.5 M; mole fraction of D2EHPA in mixture was 0.6; [Co(II)] = 500 mg·L^{-1}; diluent: kerosene; O/A = 1:1. IL ALi-D2: IL was synthesized by Aliquat 336 and D2EHPA.

Using IL as an extractant, Co(II) extraction percentage increases from 7.7 to 100% with the increase in solution pH from 1 to 2 and then constant (with the increase of equilibrium pH from 3.56 to 7.25) (Figure 1). This can be ascribed to the extraction of hydrogen ions by IL, leading to an increase in pH_{eq}, and thus extraction percentage was greatly improved. The extraction reaction of Co(II) and hydrogen ions by IL ALi-D2 can be expressed as Equations (3) and (4) [18]. Emulsion formation was also observed during the extraction at pH 4 and 5, which can be ascribed to an amphiphilic behavior of component ions.

$$2R_4NA_{(o)} + Co^{2+}{}_{(a)} + 2Cl^-{}_{(a)} \leftrightarrow 2R_4NCl_{(o)} + CoA_{2(o)} \quad (3)$$

$$2R_4NA_{(o)} + H^+{}_{(a)} + Cl^-{}_{(a)} \leftrightarrow (R_4NA)_2{\cdot}HCl_{(o)} \quad (4)$$

where subscript a and o represent the aqueous and organic phase, respectively.

The extraction percentage of Co(II) by the mixtures of D2EHPA and Alamine 336/Aliquat 336 was negligible in the pH_{eq} range of 1–5 (the pH_{eq} range of 0.67 to 3.7, respectively) (see Figure 1 and Table 2). This agrees well with the previous work that Co(II) was insignificantly extracted by single D2EHPA or mixture of D2EHPA and Alamine 336 from aqueous chloride solution when the equilibrium pH is lower than 5 [2,23,24]. The extraction of hydrogen ions by the mixture of Alamine 336 and D2EHPA can occur through either the amine salt which forms through the strong interaction of Alamine 336 and D2EHPA or the protonation of Alamine 336 [4]. The highest equilibrium pH by the mixture of Alamine 336 and D2EHPA was 3.7 (Table 2). The reactions occurring during the extraction of Co(II) by the mixtures can be represented as Equations (5)–(7).

$$R_3N_{(o)} + HA_{(o)} \leftrightarrow R_3N{\cdot}HA_{(o)} \quad (5)$$

$$H^+{}_{(a)} + R_3N_{(o)} \leftrightarrow R_3NH^+{}_{(o)} \quad (6)$$

$$R_3N{\cdot}HA_{(o)} + H^+{}_{(a)} + Cl^-{}_{(a)} \leftrightarrow R_3N{\cdot}HCl_{(o)} + HA_{(o)} \quad (7)$$

where R_3N denotes Alamine 336.

As a consequence, control of the equilibrium pH is important to enhance the extraction percentage of Co(II).

3.1.2. Effect of Interactions of the Components in Mixture on Co(II) Extraction

In another aspect, the structure of the amine and the acidic extractants can be changed in their mixtures when an interaction occurs and the formation of adducts has a certain effect on the metal extraction [1,21]. According to Liu et al., three kinds of interaction may occur between acidic and amine extractant such as (i) ion pair ($R_3NH^+A^-$), (ii) hydrogen bonding (R_3NH-A), and (iii) binding which has an intermediate characteristic as represented by the location of the proton [5]. Similarly, the interactions such as dipole interaction, hydrogen bonding, and ion pair are proposed for mixed extractants of D2EHPA and Aliquat 336 on the basis of molecular chemistry [20]. Thus, the strong interactions can be responsible for the decrease in the effective concentration of D2EHPA which act as an extractant, resulting in low extraction percentage of Co(II). Besides that, the amine salts or ionic liquids, which can be formed when the strong interaction occurs between acidic extractant (D2EHPA) and Alamine 336/Aliquat 336, can take part in the extraction reaction [4,20]. However, their amount in these mixtures may be not enough for efficient extraction of Co(II) in our experimental conditions. Apart from the formation of ILs, the release of HCl from the organic phase should be also considered. When the reverse reaction of Equation (7) occurs, the concentration of HCl in the aqueous phase would increase, resulting in low extraction percentage of Co(II) [8,22]. The reaction for the formation of IL and the transfer of HCl can be proposed as Equation (8) [20].

$$HA_{(o)} + R_4N^+Cl^-{}_{(o)} \leftrightarrow R_4N^+A^-{}_{(o)} + H^+{}_{(a)} + Cl^-{}_{(a)} \quad (8)$$

3.1.3. Effect of Mole Fraction of D2EHPA and Mixture Concentration on Co(II) Extraction

Mole fraction of D2EHPA in the mixture with Alamine 336/Aliquat 336 has a great effect on the interaction occurring in the mixture [6,20]. To investigate the effect of mole fraction of D2EHPA in the mixture on Co(II) extraction, experiments were done by varying mole fraction of D2EHPA from 0.2 to 0.8. Figure 2 shows that extraction percentage of Co(II) gradually decreased with the mole fraction of D2EHPA in the mixture with Alamine 336 but linearly increased in the case of the mixture of D2EHPA and Aliquat 336. The significant difference occurred at 0.2 mole fraction of D2EHPA in each mixture. Namely Co(II) extraction percentage by the mixture of D2EHPA and Alamine 336 was higher than 10 times to that by the mixture of D2EHPA and Aliquat 336. Based on previous works, the extraction percentage of Co(II) by pure Alamine 336/Aliquat 336 was negligible in the weak acidic conditions [2,10,25]. Thus, D2EHPA was considered to be the main extractant for Co(II) in these experiments. Furthermore, equilibrium pH was measured to understand the role of each component in the mixture. The equilibrium pH values are displayed in Table 3. From these results, the evident difference in Co(II) extraction by the two mixtures can be explained as follows.

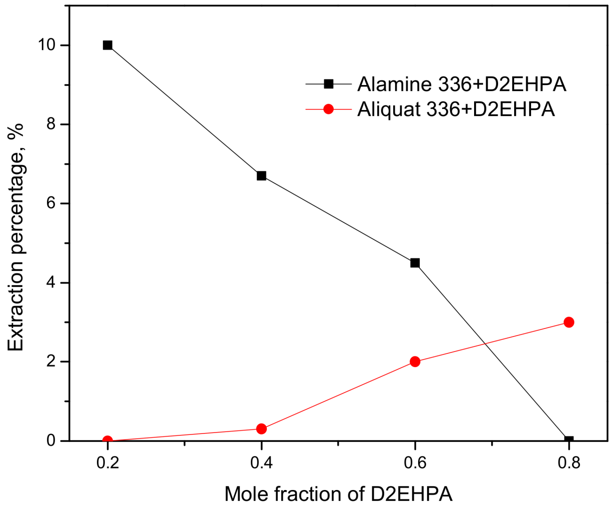


Figure 2. Effect of mole fraction of D2EHPA on Co(II) extraction by 0.5 M mixture of D2EHPA/Alamine 336 and D2EHPA/Aliquat 336. Conditions: initial pH = 2; [Co(II)] = 500 mg·L^{-1}; diluent: kerosene; O/A = 1:1.

Table 3. Variation of pH after Co(II) extraction by mixture of D2EHPA/Alamine 336 and D2EHPA/Aliquat 336.

Mole Fraction of D2EHPA in Mixture	**Alamine 336 + D2EHPA**		**Aliquat 336 + D2EHPA**	
	%E	**pH$_{eq}$**	**%E**	**pH$_{eq}$**
0.2	10.0	3.28	0.0	1.12
0.4	6.7	3.07	0.3	1.0
0.6	4.5	2.3	2.0	0.92
0.8	0.0	1.99	3.0	0.91

note: initial pH was 2; concentration of mixtures was kept at 0.5 M.

In the case of mixture of D2EHPA and Alamine 336, the equilibrium pH decreased with the increase of D2EHPA concentration in the mixture. At 0.2 mole fraction of D2EHPA (0.1 M), equilibrium pH was the highest (3.28). This indicates that Alamine 336 might extract hydrogen ion which is released from D2EHPA during Co(II) extraction, leading to an increase in equilibrium pH [2,3,26]. Consequently, the highest extraction performance was obtained at this condition (Table 3 and Figure 2). When mole fraction of D2EHPA increases, both pH$_{eq}$ and Co(II) extraction percentage decreased. This can be explained by the decrease of pH$_{eq}$ which can affect the extraction performance [2]. In the case of

0.5 M mixture of D2EHPA and Aliquat 336, the increase in Co(II) extraction percentage was negligible (Figure 2). Table 3 shows that the equilibrium pH was lower than the initial pH. The more D2EHPA present in the mixture, the lower equilibrium pH obtained after extraction. When equilibrium pH is lower than 1.0, it is difficult to extract Co(II) by the mixture of D2EHPA and Aliquat 336.

Figure 3 shows that the Co(II) extraction percentage decreased rapidly when the concentration of the mixture of D2EHPA and Alamine 336 increased from 0.5 to 2.0 M in which mole fraction of D2EHPA was fixed at 0.2. The Co(II) extraction efficiency was negligible at 2.0 M of the mixture. In the case of the mixture of D2EHPA and Aliquat 336, the Co(II) extraction percentage was less than 3% in the range of 0.5 to 2.0 M. There may be several kinds of interactions between D2EHPA and Aliquat 336 which can greatly affect the extraction role of D2EHPA. Also, the interaction between the components significantly depends on the composition of the binary mixtures, resulting in an impact on the extraction behavior of metal ions [1,20].

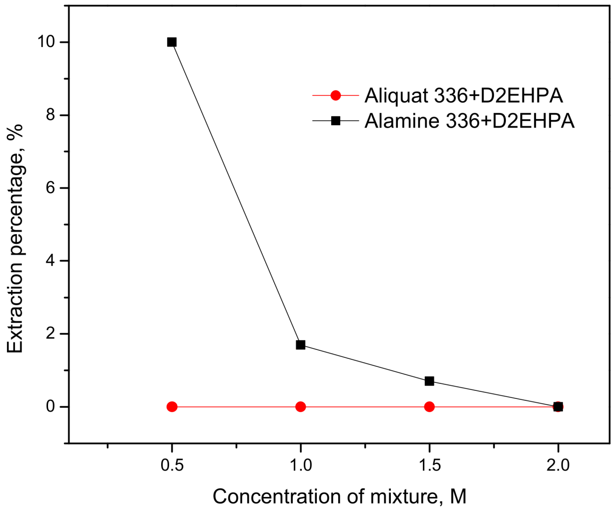


Figure 3. Effect of concentration of mixtures on Co(II) extraction. Conditions: initial pH = 2; [Co(II)] = 500 mg·L^{-1}; [mixture] = 0.5–2.0 M; diluent: kerosene; mole fraction of D2EHPA in the mixture was 0.2; O/A = 1:1.

The evident difference in extraction percentage of the mixture of D2EHPA and Alamine 336/Aliquat 336 at 0.5 M mixture can be explained by two reasons. First, ILs can form in the mixture of D2EHPA and Aliquat 336 and the presence of ILs affects the interaction between the components in the mixture [21]. When the mole fraction of ILs formed in the mixture is low, ion-dipole interaction between the chloride ion of Aliquat 336 and D2EHPA as well as hydrogen bond between D2EHPA and IL can occur [8,21]. In addition, a kind of interaction such as $[Cl]^-/[HA]/[R_4N^+]$ in which D2EHPA (HA) was kept between the ion pair of chloride anions and ammonium cations, might act against metal extraction [8,21]. Second, the difference in the stoichiometry of these two systems (mixture of D2EHPA and Alamine 336/Aliquat 336) may be responsible for the difference in extraction performance [8]. In contrast, strong interactions between the components in systems containing Alamine 336, such as electrostatic, van der Waals, and induction interactions could contribute to the stability and hydrophobicity of the extracted complexes [1,8,20,27]. In particular, the hydrogen bonds of D2EHPA in dimeric form can be broken when strong interactions between Alamine 336 and D2EHPA occur, leading to an improvement in the extraction ability of D2EHPA. These results lead to the deduction that the extraction efficiency of the mixtures can be achieved through various adjustable intermolecular interactions of mixed extractant and strongly depends on the properties as well as mole fraction of the extractants.

3.2. Variation of the pH_{eq} by Single D2EHPA and the Mixtures

In these experiments, the concentration of D2EHPA was varied from 0.1 to 0.4 M while that of the mixtures was varied from 0.5 to 2.0 M, in which mole fraction of D2EHPA was fixed at 0.2. The concentration of Co(II) was 500 mg·L^{-1} and the initial solution pH was fixed at 2. Firstly, the extraction of Co(II) by single D2EHPA in the concentration range from 0.1 to 0.4 M was obtained as a basis for comparison. The data in Table 4 shows that extraction percentage of Co(II) slightly increases as the concentration of D2EHPA increases while the equilibrium pH decreases. The decrease of equilibrium pH can be ascribed to the release of hydrogen ions from D2EHPA. According to Table 4, the equilibrium pH is lower than the initial pH even though no Co(II) was extracted into single D2EHPA and the mixture. This indicates that some of D2EHPA has been dissolved and thus the equilibrium pH is lowered.

Table 4. Variation of pH after Co(II) extraction by D2EHPA and mixture extractants.

Concentration of D2EHPA	D2EHPA		Concentration of Mixture	Alamine 336 + D2EHPA		Aliquat 336 + D2EHPA	
M	%E	pH_{eq}	M	%E	pH_{eq}	%E	pH_{eq}
0.1	0	1.96	0.5	10.0	3.3	0	1.1
0.2	0	1.94	1.0	0.7	4.13	0	0.98
0.3	1.4	1.86	1.5	1.7	4.61	0	0.89
0.4	2.5	1.80	2.0	0	4.94	0	0.93

note: initial pH = 2; [Co(II)] = 500 mg·L^{-1}; diluent: kerosene; O/A = 1:1.

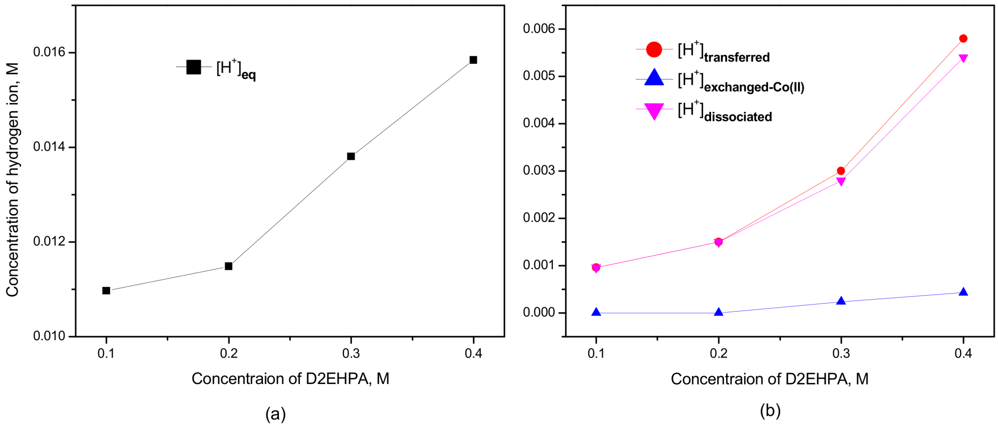
In the case of the mixture of D2EHPA/Alamine 336 and D2EHPA /Aliquat 336, the change in equilibrium pH was opposite to each other. Namely the equilibrium pH by the mixture of D2EHPA and Alamine 336 was higher than that by single D2EHPA, while the reverse was true for the mixture of D2EHPA and Aliquat 336 (see Table 4). From the initial and equilibrium pH values, the concentration of hydrogen ions was calculated on the assumption that the activity coefficient of hydrogen ion was unity. When there is free D2EHPA in the mixture, the change in the concentration of hydrogen ion during the reaction results from two effects; the first is the release of hydrogen ion from D2EHPA and the second is the dissolution of D2EHPA. Therefore, the following equation can be derived for the equilibrium concentration of hydrogen ion during the extraction of Co(II) by single D2EHPA and the mixture of D2EHPA and Aliquat 336. During the extraction with the mixture of D2EHPA and Aliquat 336, hydrogen ions can be transferred into the aqueous phase owing to the formation of IL as represented in Equation (8). Therefore, the concentration of hydrogen ions transferred from the organic during the extraction of Co(II) consists of three terms as represented in the following equation.

$$[H^+]_{eq} = [H^+]_{initial} + [H^+]_{transferred} \tag{9}$$

$$[H^+]_{transferred} = [H^+]_{exchanged\text{-}Co(II)} + [H^+]_{dissociated} + [H^+]_{from\ ILs} \tag{10}$$

Denote. $[H^+]_{exchanged\text{-}Co(II)}$ = $[H^+]$ was exchanged from Co(II) extraction; $[H^+]_{dissociated}$ = $[H^+]$ dissociated from D2EHPA which dissolved in aqueous phase; $[H^+]_{from\ ILs}$ = [HCl] was released from the formation of ILs when interaction between D2EHPA and Aliquat 336 occur.

First, the concentration of dissolved hydrogen from single D2EHPA can be obtained from the data in Table 4. Since the concentration of hydrogen ions released from D2EHPA is related to the extraction of Co(II), the hydrogen concentration corresponding to this can be obtained from the extraction data of Co(II). Figure 4a represents the variation in the equilibrium concentration of hydrogen ion against the initial concentration of D2EHPA. According to Table 4, the extraction percentage of Co(II) by single D2EHPA was negligible in these experimental conditions and thus the increase in concentration of hydrogen ion after extraction can be ascribed to the dissolution of D2EHPA during the extraction. Figure 4b clearly shows that the dissolution of D2EHPA is responsible for the change in the concentration of hydrogen ion during the extraction with single D2EHPA.



(a) (b)

Figure 4. The change of concentration of hydrogen ions in the aqueous phase after Co(II) extraction with D2EHPA. (**a**) The change of equilibrium concentration of hydrogen ions, (**b**) the change of concentration of $[H^+]_{transferred}$, $[H^+]_{exchanged\text{-}Co(II)}$ was exchanged from Co(II) extraction, $[H^+]_{dissociated}$ from D2EHPA which dissolved in aqueous phase. Conditions: [D2EHPA] = 0.1–0.4 M; diluent: kerosene; A/O = 1:1; initial pH 2.

In the case of the extraction with the mixture of D2EHPA and Alamine 336, equilibrium pH values increased with the increase in the concentration of the mixture. Figure 5 indicates that hydrogen ions in aqueous phase can be effectively extracted by the mixture of D2EHPA and Alamine 336. The extraction percentage of hydrogen ion increased from 95.0 to 99.3% when the concentration of the mixture increased from 0.5 to 1.0 M (the concentration of D2EHPA increased from 0.1 to 0.2 M). Most of the hydrogen ions were extracted when the concentration of the mixture was 1.0 M. The quantitative extraction of hydrogen ions leads to an increase in the equilibrium pH. The protonation of the amine was responsible for the extraction of hydrogen ions.

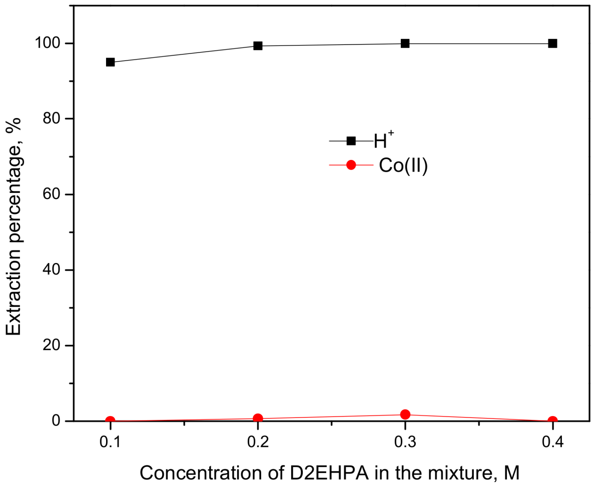


Figure 5. Effect of concentration of mixture Alamine 336 and D2EHPA on extraction of hydrogen ions in the aqueous phase and Co(II) extraction. Conditions: [mixture] = 0.5–2.0 M (in which: [D2EHPA] = 0.1–0.4 M); diluent: kerosene; A/O = 1:1; initial pH 2; [Co(II)] = 500 mg·L^{-1}.

According to Table 4, the equilibrium pH of the solution after extraction with the mixture of D2EHPA and Aliquat 336 was the lowest among the three kinds of extractants. Considering the fact that no Co(II) was extracted by this mixture and Aliquat 336, the increase in the equilibrium concentration of hydrogen ion is due to the dissolution of D2EHPA as well as the release of HCl during the formation of ionic liquid in this mixture as represented in Equation (8). In applying the mass balance Equation (10), the concentration of the hydrogen ion dissolved from D2EHPA was obtained from the data represented in Figure 4b. Then the concentration of hydrogen ion which was released from the formation of ionic liquid can be calculated from the difference between the total concentration of hydrogen ion and the concentration of hydrogen ion dissolved from D2EHPA. The calculated results are represented in Figure 6, showing that the release of hydrogen ion owing to the formation of ionic liquid in the mixture is responsible for the change in the equilibrium concentration of hydrogen ion during the extraction with mixture of D2EHPA and Aliquat 336. ILs can form in the mixture of D2EHPA and Aliquat 336 when the mole fraction of D2EHPA in the mixture was 0.2 [20] and thus the hydrogen ions can be extracted into the organic phase by these ILs [18]. Besides, the formation tendency of IL was reduced in our experiments when the concentration of the mixture increased. In addition, hydrogen bond between the hydrogen in the methyl group of Aliquat 336 and P=O group of D2EHPA can occur [20]. These can be the cause of a decrease in percentage of D2EHPA which was transformed into IL when the total concentration of mixture increased. These results are represented in Table 5.

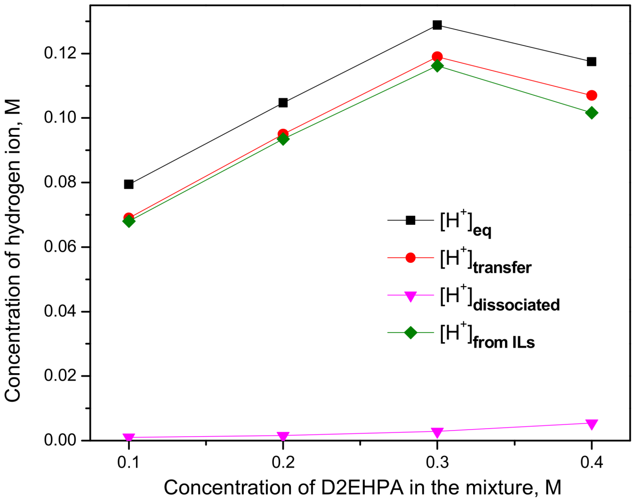


Figure 6. The change of concentration of hydrogen ion in the aqueous phase after Co(II) extraction with mixture of Aliquat 336 and D2EHPA. Conditions: [mixture] = 0.5–2.0 M (in which: [D2EHPA] = 0.1–0.4 M); diluent: kerosene; A/O = 1:1; initial pH 2.

Table 5. Results on percentage of D2EHPA was transformed into IL.

[D2EHPA + Aliquat 336], M	[D2EHPA] in Mixture, M	Percentage of D2EHPA Transformed into IL, %
0.5	0.1	68.0
1.0	0.2	46.8
1.5	0.3	38.6
2.0	0.4	25.5

In summary, the basic difference in the extraction of Co(II) between ILs and the mixture of D2EHPA and Aliquat 336 is the presence of HCl transferred from the organic phase which acts against metal extraction. Namely in Co(II) extraction with IL, no HCl is transferred from the organic into aqueous, while some of HCl should be transferred to the aqueous phase owing to the formation of IL in the case of the mixture. Therefore, it is better to employ synthesized ILs instead of using the mixture in terms of the control of solution pH.

3.3. Comparison of the Characteristics of the Extractants by FT-IR Spectra

To confirm the formation of ILs and explore their behavior in the binary mixture of D2EHPA and Aliquat 336, FT-IR spectra of this mixture and synthesized IL (IL ALi-D2) were analyzed and compared. The binary mixture samples were prepared by shaking 0.5 M mixture of D2EHPA (0.6 mole fraction) and Aliquat 336 in kerosene as a diluent. The comparison in the characteristic bands of

ILs between the mixtures and the synthesized ILs was recorded before/after extraction. The results are shown in Figure 7 and Table 6. The spectra of the extractants were observed in the region of 2000–700 cm^{-1}. The FT-IR of both the mixture and synthesized ionic liquid quite agreed well with each other. This confirms that ionic liquids could be formed in the mixture of D2EHPA and Aliquat 336, which was verified by the shift of characteristic peak of P-OH and P=O groups [18]. The difference in the intensity of the groups such as P=O and P-O-H may be due to the difference in the concentration of ILs in each sample. The formation of ILs which can extract hydrogen ions in aqueous phase is responsible for the decrease in the concentration of hydrogen ion transferred when concentration of the mixture of D2EHPA and Aliquat 336 was over 1.5 M. Indeed, there was a change in the characteristic bands of the binary mixtures of D2EHPA and Aliquat 336 before and after extraction, denoting that ILs have a strong tendency to interact with hydrogen ions in aqueous phase. In particular, the shift of P-OH and P=O group from 1236 to 1246 cm^{-1} and 1031 to 1035 cm^{-1}, respectively. All of these changes in P=O and P-OH bands may be attributed to the interaction between the oxygen atoms of the functional group of organophosphate anions and the hydrogen ions.

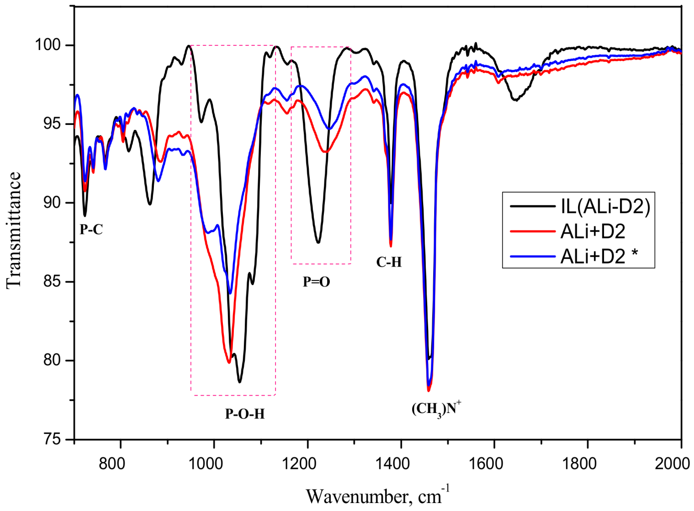


Figure 7. Comparison on the FT-IR of mixture of D2EHPA and Aliquat 336 with IL ALi-D2. Conditions: [mixture] = [IL] = 0.5 M (in which mole fraction of D2EHPA is 0.6); diluent: kerosene; A/O = 1:1; pH = 2; [Co(II)] = 500 mg·L^{-1}. ALi+D2: mixture of Aliquat 336 and D2EHPA after mixing and interactions occur; ALi+D2 *: mixture of Aliquat 336 and D2EHPA after extraction.

Table 6. Frequencies of characteristic vibrational bands of binary mixtures and IL ALi-D2.

Binary Mixture	P=O (cm^{-1})	P-C (cm^{-1})	P-O-H (cm^{-1})	C-H (cm^{-1})	$(CH_3)^+N$ (cm^{-1})
Aliquat 336 + D2EHPA	1236	723	1031	1378	1463
Aliquat 336 + D2EHPA after extraction	1246	723	1035	1378	1463
IL ALi-D2	1221	723	1053	1378	1463

3.4. The Competition in the Extraction of Hydrogen Ion and Co(II) by Using IL ALi-D2

It has been reported that the synthesized ILs derived from Aliquat 336 can extract well specific metal ions as well as hydrogen ion in the aqueous phase due to their dual function [3,18]. To investigate the extraction tendency of both Co(II) and hydrogen ions, experiments were done by varying the concentration of IL ALi-D2 from 0.1 to 0.5 M. The concentration of Co(II) in the aqueous phase was 500 mg·L^{-1} and the initial pH was kept at 2. Equilibrium pH steadily increased as the concentration of IL ALi-D2 increased from 0.1 to 0.5 M (Table 7). From these data, extraction percentage of hydrogen ion can be calculated and displayed in Figure 8. The extraction behavior of Co(II) and hydrogen ions was significantly different. Co(II) extraction percentage linearly increased when the concentration of IL

ALi-D2 increased from 0.1 to 0.5 M. At 0.1 M ALi-D2, only 3.2% of Co(II) was extracted, but complete extraction of Co(II) was possible with 0.5 M IL. This means that Co(II) extraction greatly depends on the concentration of IL (ALi-D2).

Table 7. The change of pH after Co(II) extraction process with IL ALi-D2.

Concentration of IL (ALi-D2), M	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
pH_{eq}	4.26	5.16	5.59	5.97	6.52

note: initial pH = 2; [Co(II)] = 500 $mg \cdot L^{-1}$; diluent: kerosene; O/A = 1:1.

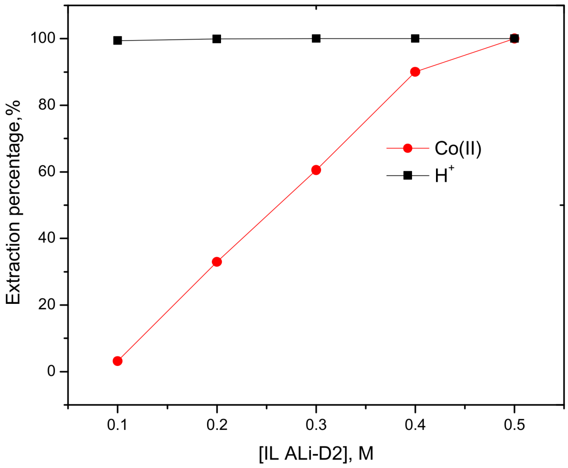


Figure 8. Effect of concentration of IL (ALi-D2) on Co(II) and hydrogen ions extraction at pH 2. Conditions: [IL] = 0.1–0.5 M; diluent: kerosene; A/O = 1:1; [Co(II)] = 500 $mg \cdot L^{-1}$.

Compared to Co(II) extraction, most of the hydrogen ions (over 99.4%) were extracted by 0.1 M IL ALi-D2 (Figure 8). When IL concentration was from 0.2 to 0.5 M, the hydrogen ion was completely extracted into the organic phase. It can be said from these results that the mixture of Aliquat 336 and D2EHPA negligibly extracted Co(II) due to the formation of IL which has a strong tendency for the extraction of hydrogen ions. From these analyses, it can be inferred that: (i) the formation of IL in the mixture of D2EHPA and Aliquat 336 suppresses the extraction of Co(II); (ii) the occurrence of the competition for the extraction between Co(II) and hydrogen ion. Also, strong interaction between Aliquat 336 and D2EHPA might depress the extraction capacity of D2EHPA for Co(II).

4. Conclusions

The comparison of the Co(II) extraction behavior between the mixture of D2EHPA/Alamine 336, D2EHPA /Aliquat 336 and their synthesized IL ALi-D2 were investigated. Extraction data showed that Co(II) extraction by these extractants significantly depended on solution pH, characteristics of interactions in the mixture, and concentration of the extractants. The strong interaction between components in the binary mixture of D2EHPA and Alamine 336/Aliquat 336 is unfavorable for Co(II) extraction. Meanwhile, IL can completely extract Co(II) from weak acid media in the equilibrium pH range from 6.52 to 7.25. The FT-IR spectra showed the difference in the characteristics of the mixtures and ILs. The tendency of the formation of amine salt/ionic liquid between D2EHPA and Alamine 336/Aliquat 336 was verified from the analysis of the extraction of Co(II) and hydrogen ion. The basic difference in the extraction efficiency of Co(II) between ILs and the mixture of D2EHPA and Aliquat 336 lies in the negative effect of HCl transferred from the organic phase. It could be said that the employment of synthesized ILs for the extraction of metal ions was better than the mixture in terms of control of solution pH. The extraction efficiency of metal with mixture extractants could be improved by adjusting the composition of mixtures.

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