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Application of bifunctional ionic liquids for extraction and separation of Eu³⁺ from chloride medium

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Abstract: The extraction of Eu^{3+} from chloride medium using bifunctional ionic liquid extractants (Bif-ILEs) tri-n-octylmethyl ammonium bis(2-ethyl hexyl) phosphate ([A336][D2EHP]) and trihexyltetradecyl phosphonium bis(2-ethylhexyl) phosphate ([P₆₆₆₁₄][D2EHP]) in kerosene was studied to develop environmentally friendly extraction process. The extraction behavior of Eu^{3+} was examined by varying key process parameters. The extraction behavior indicates that ammonium-based ionic liquid [A336][D2EHP] shows better extraction efficiency of Eu^{3+} than that of phosphonium-based ionic liquid [P₆₆₆₁₄][D2EHP]. Quantitative extraction of Eu^{3+} is obtained with 0.05 mol/L [A336][D2EHP], whereas, 0.1 mol/L of [P₆₆₆₁₄][D2EHP] is required to achieve the same extraction rate of Eu^{3+} . The extraction process is endothermic with respect to [A336][D2EHP]. Stripping experiments indicate that 100% of Eu^{3+} can be back extracted from both the loaded ionic liquids using 20 vol.% HNO₃. The highest separation factor ($\beta_{Y/Eu}$) of 653.59 is reported at pH of 3.2, and the separation factor of Eu^{3+} is 30.6 at the same pH. From the leach liquors of waste tube light powder, 99.98% of Eu and 99.99% Y are recovered using 0.2 mol/L [A336][D2EHP] in 2-stage cross current extraction with aqueous to organcic ratio (O/A) of 1:1 and 1:2.

Key words: europium; bifunctional ionic liquid; solvent extraction; separation; phosphor powder

1 Introduction

Rare earth elements (REEs) such as La–Lu are employed in the various sustainable technologies like catalysts, batteries, alloys, lighting and ceramic industry [1,2]. Separation of REEs is quite difficult because of their chemical resemblance, hence solvent extraction (SX) is one of the effective separation techniques employed for rare earth metals with high purity. Room temperature ionic liquids (RTILs) are ionic salts mainly consisting of bulky organic cations and inorganic or organic anions [3,4]. Binary extractants consisting of quaternary ammonium or phosphonium cation are great interest for researcher due to efficient extraction and separation of REEs [5,6]. Ammonium-

based bifunctional ionic liquid extractants (Bif-ILEs) such as ([N₁₈₈₈][POAA]) are used for extraction of REEs and the extraction process is compared with conventional extractant (2,6-dimethylheptyl) phenoxy acetic acid (HPOAA) [7]. The various parameters such extraction as temperature, concentration of extractants and stirring speed, have been investigated. [A336][P507] and [A336][P204] are two types of ammonium type TSILs diluted in n-heptane employed for solvent extraction of REEs from nitrate and chloride media [8]. Using both ILs heavy rare earth elements (HREEs) separation is efficient from nitrate medium and light rare earth elements (LREEs) separation is effective from chloride medium. Both phosphonium and ammonium based ionic liquids such as Cyphos IL 104 and [A336/Cy272] diluted in toluene are

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employed for liquid-liquid extraction of Y³⁺ into chloride and nitrate media [9]. Different extraction parameters are studied and the separation of yttrium from cerium and lanthanum are investigated. HNO3 is tested to be the best stripping agent for Y^{3+} from both the ionic liquids phases. Ammonium type ionic liquids like [OcGBOET][DHDGA] and [A336][DHDGA] are employed for extraction and separation of Eu and other REEs from nitric acid medium [10]. The extraction efficiency of Eu^{3+} is studied by varying extraction parameters such as acidity of aqueous medium, Eu³⁺ concentration, temperature and nature of organic diluents. Extraction of Eu³⁺ is negatively influenced by acidity of aqueous medium. Optimum extraction of Eu^{3+} is obtained with both the extractants in pH range of 4–4.5. Ionic liquids [A336][DEHP] and [A336][DGA] are diluted in various molecular diluents employed for solvent extraction of Eu³⁺ [11]. Extraction of Eu³⁺ is increased with increase in pH of aqueous medium. Extraction rate of Eu³⁺ is influenced by different extraction parameters like behavior of diluents, ionic liquid concentration, and pH, etc. The bifunctional ionic liquid[A336][P204] showed inner synergistic effect for extraction of Eu³⁺ [12]. From extraction experiment it has been observed that the complex form between [A336][P204] and Eu³⁺ exhibits high stability and hydrophobicity in nature. Stripping experiments and extraction mechanism were also investigated. The other researchers [13-20] investigated the solvent extraction of REEs from nitrate and chloride media respectively using ammonium type Bif-ILs.

In this work, the synthesized Bif-ILs, i.e., methylammonium bis(2-ethylhexyl) tri-n-octyl phosphate [A336][D2EHP] and trihexyl teteadecylphosphate phosphonium bis(2-ethylhexyl) [P66614][D2EHP] are employed for extraction of Eu³⁺ from aqueous chloride medium. The extraction properties of Eu³⁺ are compared using both phosphonium and ammonium based ILs with various extraction parameters such as pH of aqueous medium, concentration of ILs, europium ion and salting out agent concentration. Extraction mechanism, temperature effect and stripping process are also investigated. Separation of europium from REMs mixture solution is studied and then it is extended to recover Eu and Y from

waste tube light phosphor powder.

2 Experimental

2.1 Chemicals and reagents

Aqueous solution of europium was prepared by dissolving its oxide (Eu₂O₃, 99.9%, sigma-Aldrich) with small volume of concentrated hydrochloric acid. The need concentration of required different europium for extraction experiments was prepared diluting the stock solution with deionized water. Di(2-ethyl hexyl) phosphoric acid was kindly supplied by HWP, Talcher, India. Cyphos IL 101 was obtained from Cytec Solvay, Canada, as gift sample. Aliquat 336 was purchased from Sigma Aldrich in reagent grade. Bif-ILs such as tri-n-octylmethyl ammonium bis(2-ethyl hexyl) phosphate ([A336][D2EHP]) and trihexyl tetradecylphosphonium bis(2-ethylhexyl) phosphate ([P₆₆₆₁₄][D2EHP]) which were employed as extractants were prepared by ion exchange process similar to the method followed by other researcher [21,22]. The structures of the ionic liquids are represented in Figs. 1(a) and (b), respectively. Kerosene was the diluent used for reducing the viscosity of the ionic liquids.

2.2 Equilibration procedure

The extraction experiments were explored by contacting equal volume of ionic liquids (diluted in kerosene) and aqueous solution of europium chloride. The extraction studies were carried out at 298 K using 60 mL of separating funnel. After phase separation the concentration of Eu³⁺ in aqueous medium was analyzed by an Elico SI-244 UV-visible spectrophotometer with Arsenazo III and the concentration of Eu³⁺ in the organic phase was determined by mass balance method. During separation experiments the concentration of rare earth metal ions in the mixture solution was determined by ICP-MS spectrometer of Perkin Elmer model-NexION 300X. Loaded ionic liquid phase was stripped using a mineral acid such as HNO₃ with aqueous to organic ratio (O/A) of 1:1, and the aqueous strip solution is subjected to **ICP-OES** analysis.

The extraction efficiency (*E*), distribution ratio (*D*), separation factor (β) and stripping percentage (*S*) were calculated by Eq. (1):



Fig. 1 Structures of [A336][D2EHP] (a) and $[P_{66614}]$ [D2EHP] (b)

$$E = \frac{c_{\rm i} - c_{\rm f}}{c_{\rm f}} \times 100\% \tag{1}$$

Distribution ratio of rare earth metal ions (RE(III)) is interpreted as the ratio of the analytical concentration in both phases.

$$D = \frac{c_{\rm i} - c_{\rm f}}{c_{\rm f}} \tag{2}$$

$$\beta = \frac{D_1}{D_2} \tag{3}$$

$$S = \frac{[M]_{Stri}}{[M]_{Extr}} \times 100\%$$
(4)

The initial and final concentrations of rare earth metal ions (RE(III)) in aqueous medium are represented as c_i and c_f , respectively. c_i-c_f is the rare earth metal ions concentration in the ionic liquid phase. D_1 and D_2 are the distribution ratio of REs(III). [M]_{Stri} is the quantity of Eu³⁺ stripped by strippant, and [M]_{Extr} is the amount of Eu³⁺ extracted into the ionic liquid phase.

3 Result and discussion

3.1 Effect of extraction time in [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] systems

The dependence of contact time for extraction of Eu^{3+} was studied in the range 0.5–30 min. Figure 2 shows the extraction of 0.002 mol/L Eu^{3+} from chloride medium, where the pH of the aqueous medium is maintained at 3.2. Two different bifunctional ionic liquids (Bif-ILs) such as

[A336][D2EHP] and $[P_{66614}][D2EHP]$ with a concentration 0.02 mol/L were employed for the study of equilibration time on Eu³⁺ extraction. The data obtained from Fig. 2 indicate that the extraction efficiency of Eu³⁺ is increased with respect to contact time using both the Bif-ILs and 10 min is adequate for optimum extraction of Eu^{3+} . A clear phase separation is observed at 10 min of equilibration time, and after 10 min the extraction of Eu³⁺ remained unchanged. The results indicate that the extraction of Eu^{3+} is increased from 58% to 70% with extraction time from 0.5 to 10 min for [A336][D2EHP]. Similarly for phosphonium ionic liquid [P₆₆₆₁₄][D2EHP], Eu³⁺ extraction is increased from 28% to 38% with contact time from 0.5 to 10 min. The result proves that Eu^{3+} can be extracted significantly by [A3336][D2EHP]. The equilibration time of 10 min is maintained to ensure the extraction equilibrium for other experiments.



Fig. 2 Effect of equilibration time on extraction efficiency (0.002 mol/L Eu³⁺, 0.02 mol/L NaCl, pH=3.2, O/A=1:1, 0.02 mol/L [A336][D2EHP], 0.02 mol/L [P₆₆₆₁₄][D2EHP])

3.2 Effect of pH on extractability of Bif-ILs for Eu³⁺

To examine the effect of aqueous phase acidity on the extraction nature of bifunctional ionic liquids, the extraction of Eu³⁺ using [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] is found at different initial pH values of 1.3, 2.23, 3.18, 3.85 and 4.87. Figure 3 shows the comparative study of extraction of Eu³⁺ with 0.02 mol/L [A336][D2EHP] and 0.02 mol/L [P₆₆₆₁₄][D2EHP] diluted in kerosene as a function of initial pH of the aqueous phase. It is noticed that the extraction of Eu³⁺ increases as the pH of the aqueous phase increases [6,16]. Extraction efficiencies of Eu³⁺ at pH 1.3 are 12.6% and 3.8% for [A336][D2EHP] and [P₆₆₆₁₄][D2EHP], respectively, and increase to 84% and 60% at pH 4.87. This indicates that low pH has an adverse effect on the extraction tendency of Bif-ILs. It is noticed that using both the ILs at $pH_{ini} < 2.0$ the extraction of Eu³⁺ is quite low. But for $pH_{ini} > 2.0$, the extraction of Eu³⁺ is increased regularly for both the ILs [11].



Fig. 3 Effect of initial pH (pH_{ini}) on extraction of Eu³⁺ extracted by [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] (0.02 mol/L [A336][D2EHP], 0.02 mol/L [P₆₆₆₁₄] [D2EHP], 0.002 mol/L Eu³⁺, 0.02 mol/L NaCl)

By comparing the extraction of Eu^{3+} using [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] at different pH of aqueous medium, it is clear that the extraction ability of ammonium type ionic liquid [A336][D2EHP] is better than that of the phosphonium type ionic liquid [P₆₆₆₁₄][D2EHP] at high and medium pH. When the pH is low, preferential extraction of H⁺ occurs according to Eqs. (5) and (6), which decreases the effective concentration of ionic liquids in the organic phase, hence decreasing the extraction of Eu³⁺ [23].

$$H_{aq}^{+} + Cl_{aq}^{-} + \{[A336]^{+}[D2EHP]^{-}\}_{org} \Longrightarrow$$

$$[A336Cl]_{org} + D2EHPA_{org} \qquad (5)$$

$$H_{aq}^{+} + Cl_{aq}^{-} + \{[P_{66614}]^{+}[D2EHP]^{-}\}_{org} \Longrightarrow$$

$$[P_{66614}Cl]_{org} + D2EHPA_{org}$$
(6)

3.3 Effect of Bif-ILs concentration on Eu³⁺ extraction

The ionic liquid concentrations and extraction isotherm are very essential to determine the extraction mechanism. The extraction of 0.002 mol/L of Eu³⁺ at aqueous phase pH 3.2 from chloride medium using different concentrations of

ionic liquids (0.002–0.1 mol/L) diluted in kerosene was investigated. As shown in Fig. 4, the extraction efficiency of Eu³⁺ increases with the increase in concentration of both the Bif-ILs. When the extractant concentration is 0.002 mol/L the Eu³⁺ extraction is almost nil for both the extractants, i.e. 2.9% for [A336][D2EHP] and 1.1% for [P₆₆₆₁₄][D2EHP]. In the case of [A336][D2EHP], 93.6% extraction of Eu^{3+} is found with 0.025 mol/L and almost double concentration (0.05 mol/L) of [P₆₆₆₁₄][D2EHP] is needed to achieve nearly the same (94.4%) extraction of Eu³⁺. 0.05 mol/L is enough for complete (100%) extraction of Eu^{3+} with [A336][D2EHPA], while 100% extraction of Eu^{3+} is achieved using 0.1 mol/L [P₆₆₆₁₄][D2EHP]. The better extractability of ammonium type ionic liquid than that of phosphonium type ionic liquid towards Eu³⁺ could be explained on the cation size of Bif-ILs. If the alkyl chain length of cation is increased, the steric hindrance of corresponding Bif-ILs increased and extractability of ILs for Eu³⁺ decreased [5]. Since $[P_{66614}]^+$ contains longer alkyl chain than that of [A336]⁺ cation, hence extraction efficiency of [P₆₆₆₁₄][D2EHP] is less than that of [A336][D2EHPA].



Fig. 4 Effect of [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] concentration on Eu^{3+} extraction (0.002 mol/L Eu^{3+} , 0.02 mol/L NaCl, time=10 min, pH=3.2)

3.4 Stoichiometry of extracted samples

Determination of the extraction mechanism of Bif-ILs is essential to develop effective ionic liquids based extractant for solvent extraction and separation of REEs and critical metals. In the present work, slope analysis method was employed to determine the stoichiometry of Bif-ILs/Eu³⁺ complexation by plotting lg *D* versus lg [IL] at pH 3.2 (Fig. 5). The linear relationship between lg *D*

and lg [IL] is obtained with slopes of 2.91 and 2.7 for [A336][D2EHP] and [P₆₆₆₁₄][D2EHP], respectively, for the concentration of ILs from 0.002 to 0.1 mol/L. From slopes it has been confirmed that the stoichiometry of [A336][D2EHP] with Eu³⁺ and [P₆₆₆₁₄][D2EHP] with Eu³⁺ is found to be 3, which is in good agreement with the value reported by other researchers [11,12,20]. The stoichiometry of chloride ions is found to be 3 as a result of electroneutrality principle. Hence, extraction mechanism of Eu³⁺ by [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] is depicted by

$$Eu_{aq}^{3+} + 3Cl_{aq}^{-} + 3\{[A336]^{+}[D2EHP]^{-}\}_{org} \Longrightarrow$$

$$3[A336Cl]_{org} + [EuD2EHP_{3}]_{org} \qquad (7)$$

$$Eu_{aq}^{3+} + 3Cl_{aq}^{-} + 3\{[P_{66614}]^{+}[D2EHP]^{-}\}_{org} \Longrightarrow$$

$$3[P_{66614}Cl]_{org} + [EuD2EHP_{3}]_{org}$$
(8)



Fig. 5 Plot of $\lg D$ against $\lg[IL]$ for Eu^{3+} extraction by [A336][D2EHP] and [P₆₆₆₁₄][D2EHP]

3.5 Loading capacity

The most important factor in solvent extraction for an industrial point of view is that the concentration of metal ions can be loaded into the organic phase. The higher the loading capacity of extractant is, the smaller the equipment size as well as small concentration of extractant can be employed during solvent extraction experiment. The extraction tendency of Eu³⁺ was examined by varying different concentrations of Eu³⁺ in aqueous feed ranging from 0.002 to 0.02 mol/L and the pH of the aqueous phase is maintained to be 3.2. Concentration of Bif-ILs for all tests is kept at 0.025 mol/L. The loading of Eu^{3+} in the ionic increased with liquids is increasing the concentration of Eu³⁺ in the aqueous medium. After 0.008 mol/L, the metal loading capacity is almost unchanged for [P₆₆₆₁₄][D2EHP]. The loading of Eu^{3+} is increased linearly for [A336][D2EHP]. The maximum concentration of Eu^{3+} loaded using 0.025 mol/L [A336][D2EHP] is found to be 766 mg/L, by using the same concentration of [P₆₆₆₁₄][D2EHP], the Eu³⁺ loaded is found to be 455 mg/L(Fig. 6).



Fig. 6 Loading capacity of Bif-ILs (0.025 mol/L [A336] [D2EHP], 0.025 mol/L [P₆₆₆₁₄][D2EHP], pH=3.2)

3.6 Effect of sodium chloride concentration on Eu³⁺ extraction

To determine the effect of sodium chloride on Eu^{3+} extraction, the extraction of europium using [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] is performed with varying the sodium chloride concentration from 0.02 to 1 mol/L. The data for extraction of Eu^{3+} with two different Bif-ILs influenced by various concentrations of NaCl are given in Fig. 7. The extraction of Eu^{3+} extracted by both the Bif-ILs increased as the salting-out agent concentration (NaCl) increased. The increase in extraction of europium may be attributed to the participation of chloride ions in the extraction mechanism [5].



Fig.7 Effect of NaCl concentration on extraction of Eu³⁺ (0.02 mol/L [A336][D2EHP], 0.02 mol/L [P₆₆₆₁₄] [D2EHP], 0.002 mol/L EuCl₃)

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3.7 Back extraction and reusability of bifunctional ionic liquids (Bif-ILs)

Stripping process is otherwise called as back extraction, it is one of the most important aspects of liquid-liquid extraction process which check the suitability of organic extractant for industrial and practical application. Table 1 describes the suitable stripping condition for bifunctional ionic liquids. The data describe that the back extraction of Eu³⁺ is increased with the increase of acidity for stripping liquids, but this is exception for stripping of europium from [P₆₆₆₁₄][D2EHP] using sulfuric acid as strippant [22]. In the present study, the Eu^{3+} loaded ionic liquid phase prepared by using 0.05 mol/L [A336][D2EHP] and 0.1 mol/L [P₆₆₆₁₄][D2EHP] and the stripping experiments were carried out by varying different concentrations of mineral acids such as H₂SO₄ and HNO₃. From stripping experiments it has been concluded that nitric acid is the best stripping agent for stripping of Eu^{3+} from loaded [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] [24,12], and 100% stripping of europium is obtained with 20% HNO₃. With increasing the concentration of H₂SO₄ stripping of Eu³⁺ from [A336][D2EHP] is increased and 100% stripping is obtained with 20% H₂SO₄. But with increasing H₂SO₄ concentration stripping of europium from [P₆₆₆₁₄][D2EHP] is decreased and stripping percentage is reduced from 71.6% to 57.5% when the concentration of H_2SO_4 increased from 5% to 20%.

Stability and recycling property of bifunctional ionic liquids are important requirement for industrial and practical application. The reusability

Table 1Stripping of loaded [A336][D2EHP] and $[P_{66614}][D2EHP]$ with different concentrations of HNO3and H2SO4 (0.05 mol/L [A336][D2EHP], 0.1 mol/L $[P_{66614}][D2EHP]$, loaded organic [LO]=304 mg/L Eu3+)

G	Stripping percentage/%		
Stripping agent	[P ₆₆₆₁₄][D2EHP]	[A336][D2EHP]	
5% H ₂ SO ₄	71.6	75.8	
$10\% \ H_2 SO_4$	65.7	92.4	
$20\% \ H_2SO_4$	57.5	100.0	
5% HNO ₃	85	80.2	
10% HNO ₃	93.5	95.7	
20% HNO ₃	100	100	

of the Bif-ILEs [A336][D2EHP] and $[P_{66614}][D2EHP]$ in chloride medium was examined by repeated loading/stripping experiments, hence, the ILs are reused 5 times. The results given in Table 2 determine that [A336][D2EHP] and $[P_{66614}][D2EHP]$ are stable extractants because they cannot loss extraction efficiency and they can be reused for Eu³⁺ extraction [8].

Table 2 Extraction efficiency of Bif-ILEs (0.05 mol/L[A336][D2EHP], 0.1 mol/L [P66614][D2EHP], 0.002 mol/LEu³⁺, 0.02 mol/L NaCl, 20 vol.% HNO3)

Number of cycles	E[A336][D2EHP]/%	E[P ₆₆₆₁₄][D2EHP]/%
1	100	100
2	99.9	99.7
3	99.3	99.5
4	99.3	99.3
5	99.1	99

3.8 Dependence of extraction efficiency of Eu³⁺ on temperature

To investigate the important thermodynamic parameters of the liquid-liquid extraction process of Eu³⁺ by Bif-ILEs [A336][D2EHP] and [P₆₆₆₁₄][D2EHP], solvent extraction experiments of Eu^{3+} are studied over a temperature range from 30 to 50 °C. From Fig. 8 it is concluded that the extraction efficiency of Eu³⁺ is increased with temperature in the ammonium type Bif-IL system [A336][D2EHP]. The extraction efficiency of Eu^{3+} is increased from 70% to 87.2% when the temperature is increased from 30 to 50 °C using [A336][D2EHP] as an extractant. But the extraction efficiency of Eu³⁺ is decreased with increase of temperature in [P₆₆₆₁₄][D2EHP] extraction system and the extraction efficiency is decreased from 39.8% to 15.2% when the temperature is raised from 30 to 50 °C. Figure 9 presents the $\lg D$ versus T^{-1} plot having slopes of -2.278 and 2.538 for [A336][D2EHP] and [P₆₆₆₁₄][D2EHP], respectively. The ΔH^{Θ} value is calculated for [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] using the corresponding slope values according to Eqs. (9) and (10). As given in Table 3, ΔH^{Θ} value for [P₆₆₆₁₄][D2EHP] is negative, and it indicates that the extraction of Eu³⁺ is exothermic. ΔH^{Θ} value for [A336][D2EHP] is positive, and it points out the endothermic nature for extraction of Eu³⁺ by [A336][D2EHP]. The Gibbs free energy change (ΔG^{Θ}) is determined by $\Delta G^{\Theta} = \Delta H^{\Theta} - T \Delta S^{\Theta}$, and the results are given in Table 3.

$$lg D = \frac{-\Delta H^{\Theta}}{2.303RT} + \frac{\Delta S^{\Theta}}{2.303R} + 3lg[Cl^{-}] + 3\{lg c([A336][D2EHP])\} + 3lg\{c[A336Cl]\} (9)$$

$$lgD = \frac{-\Delta H^{\Theta}}{2.303RT} + \frac{\Delta S^{\Theta}}{2.303R} + 3lg[Cl^{-}] + 3lg\{c([P_{66614}][D2EHP])\} + 3lg\{c[P_{66614}Cl]\}$$
(10)



Fig. 8 Impact of temperature on extraction of Eu^{3+} (0.02 mol/L [A336][D2EHP], 0.002 mol/L [P₆₆₆₁₄] [D2EHP], 0.002 mol/L EuCl₃, pH = 3.2)



Fig. 9 Plot of $\lg D$ versus T^{-1} (0.02 mol/L [A336] [D2EHP], 0.02 mol/L [P₆₆₆₁₄][D2EHP], 0.002 mol/L EuCl₃, pH = 3.2)

Table 3 Extractive thermodynamic parameters using[A336][D2EHP] and [P66614][D2EHP] at 303 K

<u> </u>			
Extractort	ΔH^{Θ}	ΔS^{Θ}	ΔG^{Θ}
Extractant	$(kJ \cdot mol^{-1})$	$(J \cdot K^{-1} \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$
[A336][D2EHP]	43.617	181.92	-98.74
[P ₆₆₆₁₄][D2EHP]	-48.59	-145.77	-4.42

3.9 Separation of rare earth elements

Separation of REMs from each other is one of the challenging tasks because of its nearly same chemical properties [25]. Separation of heavier REEs like europium, yttrium from lighter REEs such as cerium and lanthanum is highly important because these lanthanides are together found in fluorescent lamp waste [26]. The above studies show that [A336][D2EHP] is a better extractant than $[P_{66614}][D2EHP]$. Hence, the separation behavior of REEs from synthetically prepared mixture solution was carried out by using the ammonium type Bif-IL. The synthetic mixture solution has 0.002 mol/L of each europium, yttrium, cerium and lanthanum and 0.02 mol/L sodium chloride. The concentration of the Bif-IL used for extraction experiment is 0.05 mol/L and the separation efficiency is tested by varying pH of the aqueous medium from 2.6 to 4.0 (Fig. 10). It has been observed that the extraction tendency of all the four REEs increase regularly with increase in pH of the aqueous medium, and the order of extraction is $Y^{3+} > Eu^{3+} > Ce^{3+} > La^{3+}$ [27]. The maximum extraction of yttrium and minimum extraction of lanthanum are achieved according to the ionic radii [28]. From Table 4, at initial pH 3.2, Y/Eu



Fig. 10 Affinity of [A336][D2EHP] towards light and heavy REEs at different initial pH (0.002 mol/L Y^{3+} , Eu^{3+} , Ce^{3+} and La^{3+} , 0.02 mol/L NaCl, 0.05 mol/L IL)

 Table 4 Separation factor of REEs with 0.05mol/L

 [A336][D2EHP]

Sl No.	Initial pH	β_1	β_2	β_3
1	2.6	4.44	7.60	17.79
2	3.0	151.11	7.56	20.37
3	3.2	653.59	9.68	30.6
4	4.0	466.38	10.91	29.02

 $\beta_1 = D_Y/D_{Eu}; \beta_2 = D_{Eu}/D_{Ce}; \beta_3 = D_{Eu}/D_{La}$

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separation factor is found to be the highest (653.59) and that of Eu/La is also the highest (30.6).

 Table 6 Composition of metal values in aqueous and organic phase

3.10 Recovery of Eu³⁺ and Y³⁺ from exhaust tube light phosphor powder

The exhaust fluorescent lamps are a big source of rare earth elements like Y, Ce, La, Eu, and Yb etc. The red phosphor contains a good amount of Y and Eu. In one of our previous studies, a process was developed to separate Y and Eu from the leach liquor of the exhaust tube light phosphor powder [29]. The same leaching condition is applied here to generating the leach liquor and the composition of the solution is almost same, i.e., 1888 mg/L Y, 160 mg/L Eu, 2.12 mg/L La, 2.0 mg/L Ce and 160.7 mg/L Ca. The pH of leach liquor is increased to 3.2 and that solution is subjected for ionic liquid concentration variation from 0.05 to 0.2 mol/L. The results are presented in Table 5. As the amount of Ce and La is very less in comparison to Y and Eu, they are not given in the table and there is no Ca extraction. From Table 5, it is found that the extraction of Y and Eu is increased with increase of extractant concentration. 0.2 mol/L [A336][D2EHP] is chosen which corresponds 84% and 88% of Eu and Y extraction pertaining to the loading of 134.4 mg/L Eu and 1654.4 mg/L Y to the ionic liquid phase. However, there are still 25.6 mg/L Eu and 225.6 mg/L Y remained in the aqueous phase. This requires additional extraction stage for complete removal. Counter-current extraction will not be feasible here as both of the metal extractions nearly equal. So, to remove the metals from the second stage, a cross-current extraction is carried out at O/A ratio of 1:2. From Table 6, it is found that by 2-stagecross-current extraction with O/A=1:1 and 1:2, 99.98% Eu and 99.99% Y are extracted into organic phase. The loaded organic phases are combined and both Eu and Y are stripped by using 20 vol.% HNO₃.

 Table 5 Effect of [A336][D2EHP] concentration on

 leach liquor of waste tube light phosphor powder

c([A336][D2EHP])/	Extraction efficiency/%		
$(mol \cdot L^{-1})$	Eu ³⁺	Y ³⁺	
0.05	31.9	38.2	
0.125	68.1	80	
0.2	84	88	

T	Concentration/(mg·L ⁻¹)			
Item	$\mathrm{Eu}_{\mathrm{aq}}^{\mathrm{3+}}$	$Y^{3+}_{aq} \\$	$\mathrm{Eu}_{\mathrm{org}}^{3+}$	Y_{org}^{3+}
Leach liquor	160.1	1888		
Stage 1 with O/A=1/1	25.6	225.6	134.5	1654.4
Stage 2 with O/A=1/2	0.03	0.012	51.14	451.2

4 Conclusions

(1) Europium extraction is examined with various extraction parameters using ionic liquids [A336][D2EHP] and $[P_{66614}][D2EHP]$. To achieve extraction equilibrium employing both the ionic liquids, 10 min of equilibration time is maintained.

(2) Higher pH favours extraction of europium and maximum extraction of Eu^{3+} is obtained at initial pH 4.87 by both the extractants of [A336][D2EHP] and [P₆₆₆₁₄][D2EHP].

(3) The ammonium type ionic liquid [A336][D2EHP] is found to be more effective than the phosphonium type ionic liquid [P₆₆₆₁₄][D2EHP] for extracting Eu³⁺ from chloride medium.

(4) The slope analysis method confirms the 3:1 stoichiometry of [A336][D2EHP] and $[P_{66614}][D2EHP]$ with Eu^{3+} . With two Bif-ILs systems, salting-out agent of NaCl has a favourable influence on Eu^{3+} extractability.

(5) Based on the stripping studies, it has been found that nitric acid is the best stripping agent to remove Eu^{3+} from loaded [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] and 100% removal of Eu^{3+} is viable with 20 vol.% HNO₃.

(6) The extraction process of Eu^{3+} with [A336][D2EHP] and [P₆₆₆₁₄][D2EHP] is endothermic and exothermic, respectively, according to the temperature variation.

(7) Extraction sequence of REMs using [A336][D2EHP] is $Y^{3+} > Eu^{3+} > Ce^{3+} > La^{3+}$. Highest Y/Eu separation factor (653.59) is obtained at pH 3.2 with [A336][D2EHP]. The ammonium-based IL is employed to recover both Eu and Y from waste tube light phosphor powder, and it is found that by 2-stage cross-current extraction with O/A=1:1 and 1:2, 99.98% of Eu and 99.99% Y are extracted into the organic phase using 0.2 mol/L [A336][D2EHP].

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双功能离子液体在氯化物介质中萃取分离 Eu³⁺的应用

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摘 要:研究使用双功能离子液体萃取剂(Bif-ILEs)三辛基甲基氯化铵二(2-乙基己基)磷酸酯([A336][D2EHP])和十四烷基三己基氯化膦二(2-乙基己基)磷酸酯([P66614][D2EHP])、以煤油作稀释剂从氯化物介质中萃取 Eu³⁺的过程,以开发环境友好的铕萃取工艺。通过改变关键工艺参数,研究 Eu³⁺的萃取行为。萃取研究表明,铵基离子液体 [A336][D2EHP]对 Eu³⁺的萃取效率优于膦基离子液体[P66614][D2EHP]。例如,使用 0.05 mol/L [A336][D2EHP] 可以定量萃取 Eu³⁺,而需要 0.1 mol/L 的[P66614][D2EHP]才能达到相同的 Eu³⁺萃取率。对于[A336][D2EHP],铕的 萃取为吸热过程。反萃实验表明,使用 20% HNO₃(体积分数)可以将 100%的 Eu³⁺从两种负载的离子液体中反萃下 来。在 pH 值 3.2 时,分离因子(β_{V/Eu})最高,达到 653.59;在相同 pH 值下,Eu³⁺对 La³⁺的分离因子为 30.6。采用 0.2 mol/L [A336][D2EHP]、相比 O/A=1:1和 1:2 的两级错流萃取,可从废灯管荧光粉浸出液中回收 99.98%的 Eu 和 99.99%的 Y。

关键词: 铕; 双功能离子液体; 溶剂萃取; 分离; 荧光粉

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