

## Adsorption of DY using Synergist Extractants using Ionic Liquid Immobilised on Resins

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### ABSTRACT

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In the past few years, solid liquid extraction (SLE) has shown greater potential in extraction of rare earth elements (REE) compared to liquid-liquid extraction (LLE). The objective of this study is to analyse the extraction behaviour of dysprosium (Dy) using the extractant immobilised resin (EIR) in SLE. In this study, the synergist activity between ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C2mim][NTf2]) or 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C4mim][NTf2])) with conventional extractant of Aliquat 336 (A336) were investigated and the most effective synergist extractant (SE) was further immobilised onto resins (CR11, HP20 and SP207) to synthesise EIR. Inductively coupled plasma mass spectrometry (ICP-MS) was used to detect the concentration Dy before and after extraction. Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) were used to characterise EIRs. From the study, [C2mim][NTf2] showed better compatibility with A336 since this SE (A336-[C2mim][NTf2]) gives higher extraction efficiency of Dy at 90% compared to A336-[C4mim][NTf2] with less than 11% efficiency. SLE using resins immobilised with A336-[C2mim][NTf2] proved that only EIR1 (CR11) can effectively extract Dy compared to EIR2 (HP20) and EIR3 (SP207). The porosity of CR11 was higher compared to other resins which made EIR1 very efficient in adsorbing Dy. Plus, using 0.1 g of EIR1, 100% of Dy was extracted from 5 mL of aqueous phase in SLE compared to 2 mL of aqueous phase in LLE. Conclusively, this research has the potential to improvise the conventional practise of LLE into SLE using EIR with reduction in the use of extractant.

#### Keywords:

Solid liquid extraction; liquid-liquid extraction;  
rare earth elements; ionic liquid, dysprosium;  
synergist

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## 1. Introduction

Rare earth elements (REE) ores are extracted using conventional solvent extraction method in liquid-liquid extraction (LLE) system. Solvent extraction is desirable due to convenient to operate at large scale production of REE. Though, the efficiency of REE extraction using LLE system is questionable due to the high consumption of chemicals and large production of toxic waste. Solvent extraction mostly uses conventional extractants such as Versatic 10, Napthenic acid, D2EHPA, Aliquat 336 and Cyanex 272 to extract REE [5,10,23,24]. These conventional extractants give severe environmental impact and lead to high wastewater management cost. The use of ionic liquid (IL) as an alternative extractant [1,2,16] has attracts researcher to implement the solvent in the extraction

of REE. The use of IL as extractant is beneficial in terms of giving low volatile organic compound (VOC) but gives poor extraction efficiency compared to certain conventional extractant such as D2EHPA and PC-88A [13, 22,28].

Therefore, few researchers took the initiative to combine conventional extractant with IL to synthesise new synergist extractant (SE). The SE is expected to reduce the number of extraction stages and increase the extraction efficiency [4,22,28]. Regardless, the efficiency of synergist extractant in LLE are still poor due to poor contact between extractant and desired elements. Multiple contact effort used in LLE in order to increase the contact between REE and extractant had led to other problem such as loss of extractant into aqueous phase and emulsion [14,30]. Due to the disadvantages of LLE, supported materials for extractant were considered and investigated. The most effective extractant normally immobilised onto materials such as resin, silica, membrane and microorganism and the newly synthesised extractant is known as extractant immobilised material (EIM). EIM is purposely developed to reduce losses of extractant into aqueous phase and increases the extraction efficiency of REE [3, 12,15,18,21,26].

Dysprosium (Dy) is one the REE and also known as one of the critical elements on earth [6]. Dy is expensive, very difficult to be extracted for optimum purity and has high resistance towards demagnetisation [11,25]. Not many studies concentrate on the extraction of Dy but most extraction of Dy are conducted in SLE instead of LLE. SLE system such as adsorption has the capability to adsorb desired elements from a very low concentration solution and gives higher extraction efficiency compared to other techniques.

This research studies the extraction of Dy from simulated aqueous stock solution using extractant immobilised resin (EIR). The extractant used for immobilisation is synthesised from combination of A336 (conventional extractant) with [C4mim][NTf2] or [C2mim][NTf2], respectively. Moreover, this research compares the extraction conducted in LLE with SLE in terms of the removal percentage of Dy.

## 2. Experimental

### 2.1 Materials

The ionic liquids used are 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, [C2mim][NTf2] and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, [C4mim][NTf2]. Aliquat 336 (A336) is used as the conventional extractant and the simulated aqueous phase is a solution of dysprosium (III) nitrate hexahydrate dissolved in 0.1 M of nitric acid. These chemicals were bought from Sigma-Aldrich Malaysia without further purification. Resins involved are DIAION™ CR11, DIAION™ HP20 and SEPABEADSTM SP207 which were supplied by Mitsubishi Chemical Singapore [7,11].

### 2.2 Methods

The preparation of SE between ILs and conventional extractant were based on the ratio of 1:1, 1:2, 1:3, 2:3 and 1:4 to compare the effects of ionic liquid amount in extraction of Dy. A336 and [C4mim][NTf2] were combined to synthesise SE of A336-[C4mim][NTf2] by adding certain amount of A336 into 1 mL of [C4mim][NTf2]. The mixture was shaken for few hours using mechanical shaker at 200 rpm. Then, using the same ratio and procedure, [C4mim][NTf2] was replaced with A336 [C2mim][NTf2] to formulate SE with different types IL. The performance of SEs were compared based on the extraction efficiency on Dy using LLE method. 0.01 M of Dy stock solution was mixed together with an equivalent volume of SE using mechanical shaker at 200 rpm for 10 min. The mixture was

then separated using centrifuge at 2000 rpm for 10 min. The Dy solution was analysed using ICP-MS before and after the extraction. Eq. (1) was used to calculate the extraction efficiency, E in percentage where  $C_0$  is the initial concentration and  $C_e$  is the equilibrium concentration of REE (mol/L).

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The most effective SE was then immobilisation on three types of resins (CR11, HP20 and SP207) to synthesise EIRs. Then, the EIRs were studied using SLE to make comparison on the extraction efficiency between each EIRs. In this step, 0.5g of EIR was mixed with 5 mL of Dy solution in beaker for 10 min at 200 rpm. The most efficient EIR was then used for pH study where the same SLE was repeated using different pH level. The adjustment of pH was done using sodium hydroxide. Similar to LLE, the efficiency is calculated Equation 1 where the concentration of Dy before and after extraction process is determined using ICP-MS.

### 3. Results and Discussion

#### 3.1 Liquid-Liquid Extraction (LLE) of Dy using Synergist Extractants

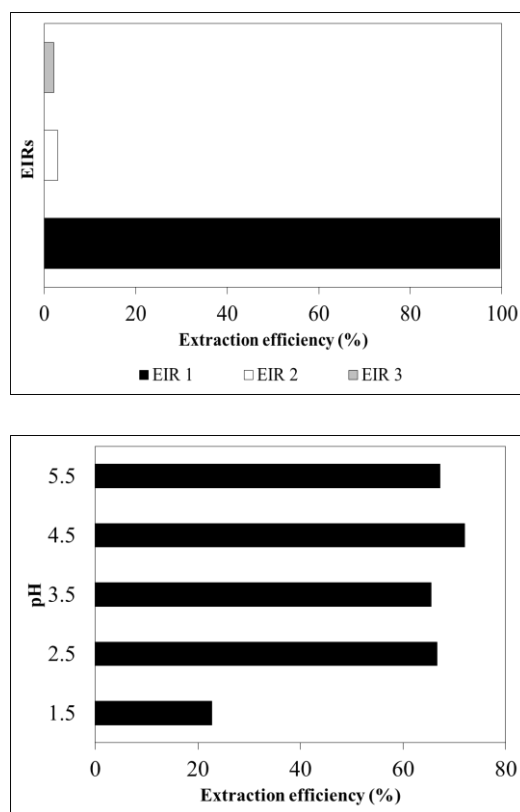
In the first stage of study, the extraction of Dy is studied by comparing the performance of the most effective SE in LLE system. There are two kinds of SE developed in this study which are A336-[C2mim][NTf2] and A336-[C4mim][NTf2] where both SE are the combination of conventional extractant (A336) and ILs ([Cnmim][NTf2],  $n = 2,4$ ), respectively. Fig. 1a shows the synergist effects between A336-[C2mim][NTf2] and A336-[C4mim][NTf2] on the extraction of Dy at different ratios.

Based on the result, there is not much different made in extraction of Dy regardless the ratios between A336 and ILs. However, A336-[C2mim][NTf2] shows better extraction ability compared to A336-[C4mim][NTf2] when the extraction efficiency is almost consistent in all ratio at the average of 89%. A336-[C4mim][NTf2] gives very poor extraction efficiency with an average of 9%. The high extraction efficiency by A336-[C2mim][NTf2] may be reflected by the effect of lower viscosity of [C2mim][NTf2] compared to [C4mim][NTf2]. Typically, lower viscosity of IL yield in better extraction of REE and has the same effects was found for this study for Dy extraction. This finding is similar to the work by Yang *et al.*, [28] where they found that higher viscosity of IL contributed to declination in the extraction efficiency of REE [28].

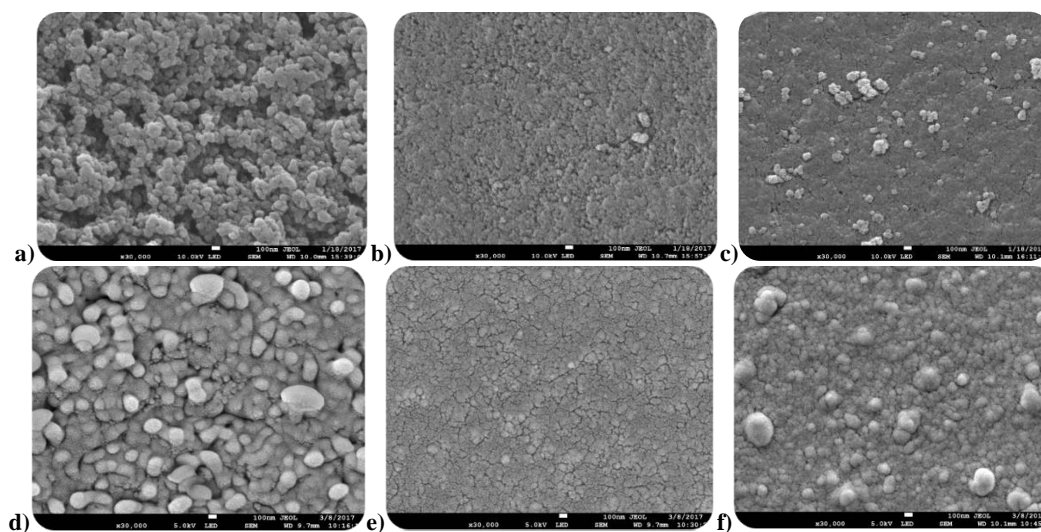
Figure 1b shows the comparison between A336-[C2mim][NTf2] at the ratio of 1:2 with other independent extractants such as C4mim, C2mim and independent A336. From the results, [C2mim][NTf2] extractant gives the highest extraction efficiency of Dy without any synergist effects. Apparently, Dy was extracted effectively using [C2mim][NTf2] compared to other extractants in Fig. 1b. This is a new finding on C2mim to have a good compatibility with Dy in LLE. Moreover, synergist effects of C2mim with A336 in this system caused the declination in extraction efficiency up to 90% compared to when C2mim is independently extract Dy. This is unusual as Cnmim is commonly more effective when synergised with other conventional extractant such as TODGA and DODGA (Yang *et al.*, 2012). On the other hand, the extraction of Dy using [C4mim][NTf2] without the synergist effect of A336 showed similar patterns with the extraction of Dy using A336-[C4mim][NTf2] and both results showed less extraction efficiency compared to [C2mim][NTf2].

The extraction efficiency of Dy using A336 independently without [C2mim][NTf2] is 60%, which was about 30% less efficient compared to when it was synergised together with [C2mim][NTf2] as shown in Fig. 1b. A336 is a conventional extractant that visibly has high viscosity (1500 mPas) and more effective in extracting REE. The main purpose of ILs in this synergist extractant is to be the diluent to the main extractant (A336). The potential of A336 is enhanced through the synergist effects

with [C2mim][NTf2] but the efficiency is pulled back when it was synergised with [C4mim][NTf2]. A further study can be conducted to understand the effects of synergist between ILs and A336.



**Fig. 1.** Extraction of Dy using extractant immobilised resin (EIR) in LLE. a) Comparison the performance of EIRs. b) Extraction using EIR1 at various pH.



**Fig. 2.** The FESEM images captured before immobilisation: a) CP11, b) HP20 and c) SP207, and after immobilisation of resins: d) EIR1, e) EIR2 and f) EIR3

Therefore, from LLE study, A336-[C2mim][NTf2] at ratio of 1:2 has been identified as the most effective SE with 90% of Dy recovery. This SE is used for further study on the extraction of Dy in SLE by immobilising A336-[C2mim][NTf2] onto resins.

### 3.2 Characterisation of Resin

The resins were analysed using FESEM before and after immobilization as shown in Fig. 2. Fig. 2a image shows clear porosity that available in CP11 resin compared to HP20 and SP207 in Fig. 2b and Fig. 2c. The condition of resin before immobilisation clearly signify the capability of each resin in extraction process. After immobilization, the resins show a sign of synergist extractant of A336-[C2mim][NTf2] wrapping the resin as per in Fig. 2d and Fig. 2f. However, only a slight visibility of the extractant detected in EIR 2 (Fig. 2e).

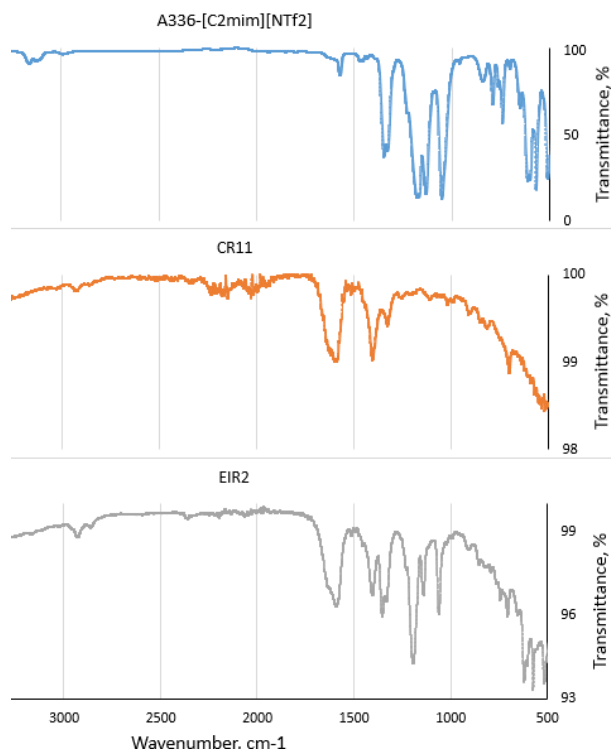
Since resin CP11 shows better extraction potential, the resin was analysed using FTIR and the reading shown in Fig. 3. The wavenumber in the fingerprint region of EIR1 shows similarity between Fig. 3a and Fig. 3c. This includes CH<sub>3</sub>, C-Cl, C-F and S=O bonds at wavelength of 1465 cm<sup>-1</sup>, 785-540 cm<sup>-1</sup>, 1400-1000 cm<sup>-1</sup> and 1300-750 cm<sup>-1</sup> respectively. Both CH<sub>3</sub> and C-Cl bonds exist in A336 whereas both S=O and C-F bonds exist in pure [C2mim][NTf2]. Regardless, no significant changes occurred on the resins after immobilisation was conducted. This was shown in the Fig. 3b and Fig. 3c where the functional group of the resin remains stable and shows no sign of reaction. This indicates that immobilisation of CP11 using A336-[C2mim][NTf2] was performed without the formation of new bonding.

### 3.3 Solid-Liquid Extraction (SLE) of dy using EIR

Figure 4a shows the result of EIRs performance in SLE using 0.5g resin respectively on 5 mL of simulated aqueous phase of Dy. EIR1 gives the most significant result compared to other resins with complete extraction of Dy. This result is co-current with the morphology analysis and manufacturer's data where EIR1 known to have a highly porous surface that is very supportive in extraction and adsorption of Dy. EIR2 and EIR3 resulted in very poor extraction of Dy mainly due to nonporous surface area which failed to adsorb Dy and A336-[C2mim][NTf2] failed to synergised effectively with the resin as shown in Fig. 2. Plus, the main function of HP20 and SP2017 resins are not suitable for metal extraction. HP20 is more practical for food and beverage processing while SP207 is practical for adsorption of fatty acids regardless both resins are highly hydrophobic (Cavaco et al., 2009, 2007). Basically, apart from effective extractant, the porosity and practical surface area of resin play important roles in adsorption of Dy.

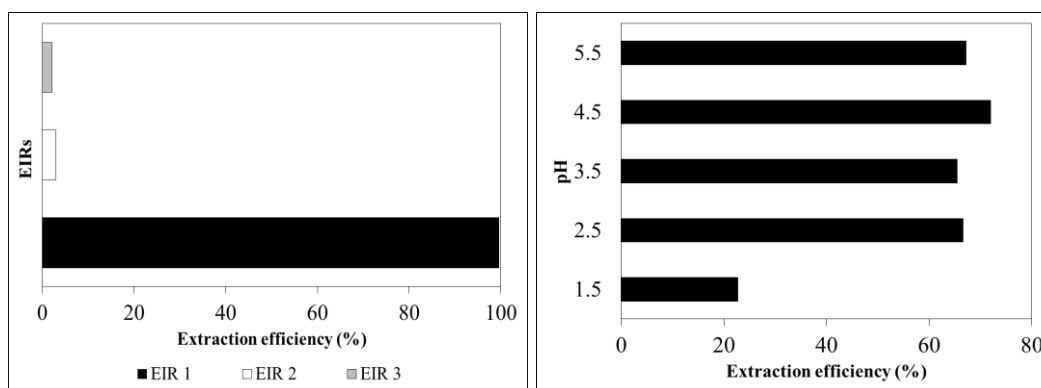
The subsequent study focus on the effect of pH level on Dy adsorption ability to identify the optimum pH condition for the process. Fig. 4b shows the extraction efficiency of Dy using EIR1 at 5 different pH values. Reflected on the performance of 0.5 g of EIR1 in Fig. 4a, the amount of EIR1 is then reduced to 0.1 g in the pH controlled extraction to study the limit of EIR1 under the influence of pH in SLE.

At the pH value of 1.5, the extraction efficiency is the lowest but increased at pH value of 2.5. The extraction of Dy using 0.1 g of EIR achieved 70% under the optimum pH of 4.5. Basically, the extraction of Dy enhance at pH in between 2.5 to 5.5. Similarly, Lee *et al.*, [15] stated that the uptake of REE from aqueous phase is optimised by setting the pH in between 3.5 to 4.5 using magnesium oxide [19,20].



**Fig. 3.** FTIR analysis on a) A336-[C2mim][NTf2], b) CR11 and c) EIR1

Extraction	pH control	Volume of extractant (mL)	Resin (g)	Volume of Dy solution (mL)	Extraction efficiency (%)
LLE	-	1.5	-	1.5	90
SLE	-	0.5	0.5	5.0	100
SLE	4.5	0.1	0.1	5.0	70



**Fig. 1.** Extraction of Dy using extractant immobilised resin (EIR) in LLE. a) Comparison the performance of EIRs. b) Extraction using EIR1 at various pH

At the optimum pH level, EIR reduced the extractant consumption up to 15 times less compared to LLE where only 3 mL of SE was used to immobilise 3 g of resin and only 0.1 g of EIR needed to extract 5 mL of Dy solution at the optimum pH. Table 1 summarised the extraction efficiency of Dy in LLE and SLE with and without pH control. Dy extraction using LLE system used a minimum 1.5 mL of SE for every 1.5 mL of Dy solution. The comparison on the consumption is big between SLE and LLE. The task of supporting resin is to increase the surface area of SE thus increases the contact area

between extractant and Dy which eventually reduce the use of extractant [9,17,27,16]. Thus, the increase in contact area between extractant and Dy was found to be proportional with the increase in Dy extraction efficiency in SLE.

#### 4. Conclusion

Studies on the uptake of Dy through LLE and SLE systems has been successfully conducted. From the result of LLE study, it was found the ratios used to synthesise SE did not have significant effect on the extraction of Dy. However, synergist extractant of A336-[C2mim][NTf2] was found to be more efficient than A336-[C4mim][NTf2] due to the lower viscosity of [C2mim][NTf2] compared to [C4mim][NTf2]. The immobilisation of A336-[C2mim][NTf2] on resins only effective on CR11 (EIR1) mainly due to the high porosity of the resin compared to HP20 and SP207. Plus, A336-[C2mim][NTf2] was well immobilised on CR11 as shown in FTIR analysis compared to the other resins without any significant change in chemical composition. The use of supporting resin reduced the amount of extractant up to 20-30 times compared to LLE due to an increase in extractant coverage and contact area between the resin and the extracted element, Dy.

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