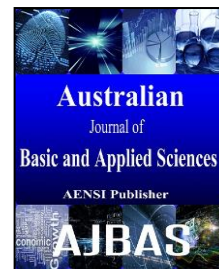




## AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414  
Journal home page: www.ajbasweb.com



### Interaction, Mechanism and Synergism of Rare Earth in [A336][DEHPA] Extraction System

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#### ARTICLE INFO

##### Article history:

Received 19 August 2016

Accepted 10 December 2016

Published 31 December 2016

##### Keywords:

Rare earth, binary mixture, ionic liquid, synergistic, interaction

#### ABSTRACT

**Background:** The synergistic effect of rare earth (RE) in binary extractant system is predominantly determined by the nature and strength of the interaction between the two extractants. In order to correlate qualitatively the interaction in the absence/presence of RE element such as samarium, FT-IR spectra for di-(2-ethylhexyl) phosphate (DEHPA) and Aliquat 336 (A336) extractants toward their precursors have been analyzed. Changes in the functional group behavior in the spectra confirmed the presence of interaction between the RE and extractants and the mechanism was revealed to be ion association. Enhancement in the distribution coefficient and synergistic effect in the binary extractant system compared to the individual extractant using solvent extraction technique towards La (III), Sm (III) and Y (III) were also observed. The highest distribution coefficient is 2.62 from the Y (III), and then followed by Sm (III) and La (III) with synergistic enhancement of 1.10 and 1.06, respectively. This work demonstrates an impeccable extractant candidate for an improved and environmental friendly RE separation in both laboratory and industrial application.

#### INTRODUCTION

Solvent extraction is the most common techniques used to separate and extract rare earth metals either from complex liquor or effluent. However, solvent extraction usually requires a high number of separation stages depending on the type of extractant and minerals used. In some cases, up to hundreds of stages required for the separation, extraction and purification of the targeted metals (Xie *et al.*, 2014). Over the years, more and more studies have been dedicated to find an alternatives to overcome this problem by replacing commonly used extractant such as di-(2-ethylhexyl) phosphoric acid (DEHPA) and 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester (EHEHPA) with another extractant that able to provide better distribution and separation properties (Preez & Preston 1992; Sun *et al.* 2005; Chen *et al.* 2015; Rout & Binnemans 2015). Tributyl phosphate (TBP) for examples, become the most preferred extractant for industrial scale operation and is proven able to separate trivalent rare earth efficiently in nitrate medium (Gupta & Krishnamurthy, 2005). Naphthenic acid also has been widely utilized by Thorium Ltd. In England and Molycorp processing plant in Colorado to purify yttrium. In Thorium Ltd processing plant, a high purity of Y<sub>2</sub>O<sub>3</sub>, 99.999% was achieved from 47% Y<sub>2</sub>O<sub>3</sub> concentrates (Gupta & Krishnamurthy, 2005).

Nowadays, ionic liquid (IL) appoints as the most leading technique in rare earth separation. The research on IL was started by Paul Walden in 1914 and now the application has extended into the industrial scale (Petkovic *et al.*, 2011). The benefit of choosing IL as an extractant are IL holds unique properties such as low volatility, low combustibility, wide liquid range, thermal stability, adjustable functional group, high conductivity and wide

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**To Cite This Article:** Nurul Ain Ismail, Anwaruddin Hisyam, Saffuan Shariff and Badhrulhisham Abdul Aziz., Interaction, Mechanism and Synergism of Rare Earth in [A336][DEHPA] Extraction System. *Aust. J. Basic & Appl. Sci.*, 10(17): 48-54, 2016

electrochemical window. In rare earth extraction, IL not only eliminates the needs of saponification process, IL also reduce the risk of combustion by removing the diluent from the process (Sun & Waters, 2014). Numerous combination of metal- IL has been reported especially for rare earth extraction (Sun *et al.* 2015; Rout, *et al.* 2014a; Rout *et al.* 2014b) and Aliquat 336 (A336) is among the promising candidate (Mikkola *et al.*, 2006; Sun *et al.*, 2011; Zhu *et al.*, 2015). In addition to the great extraction efficiency of A336, this quaternary ammonium is cheap and contain the least toxicity compared to other IL (Mikkola *et al.*, 2006; Montalbán *et al.*, 2016).

Apart from formulating new extractant, researchers also preferred to develop a binary extraction system, in which it consist of two extractants. The combination of DEHPA and EHEHPA has been extensively studied over the past decades due to the ability of this mixture to overcome the limitation in each individual extractant (Huang *et al.*, 2008; Wang *et al.*, 2011; Zhang *et al.*, 2014). The DEHPA + EHEHPA mixture contributes to an improved extractant with low acidity in stripping process and high extraction efficiency for extraction of rare earth. Currently, the combination of IL and other extractant become the main interest in separation studies for their high inner synergistic effect toward rare earth metals. The inner synergistic effect highlighted some advantages, that is, it could provide larger extraction capacity for both cation and anion in the extractant mixture (Sun, 2014). In this article, the interaction and mechanism between ionic liquid, A336 and organophosphorus acid extractant, DEHPA towards samarium (Sm) ions are studied. Moreover, the comparison of the distribution coefficient of the bifunctional IL, [A336][DEHPA] with the individual extractant such as La, Sm and Y are also explored.

## MATERIALS AND METHODS

### *Chemicals and reagents:*

Aliquat 336, (A336) and di-(2-ethylhexyl) phosphate (DEHPA) were purchased from Sigma. Nitric acid, sodium hydroxide and sodium nitrate were purchased from Fischer Scientific. Stock solution of La (III), Sm (III) and Y (III) was prepared by dissolving its oxide (99.9%) in concentrated nitric acid. All other chemicals used were of analytical grade. The [A336][DEHPA] was prepared using by acid/base neutralization method as described by (Sun *et al.*, 2010a).

### *Apparatus and measurement:*

The pH values were measured using a Mettler Toledo (MP2200) pH meter. The concentration of RE (III) in the aqueous solution was determined by inductively coupled plasma – mass spectrometry (ICP-MA) (Agilent 7500 CX, USA). The concentration of the RE (III) in the organic phase was calculated by mass balance. FTIR measurement of all the extractant was performed with a Fourier transform infrared spectroscopy – attenuated total reflectance (FTIR-ATR) (Spectrum 100, Perkin Elmer, USA)

### *Extraction Procedures:*

[A336][DEHPA] and their precursors were dissolved in cyclohexane for extraction. 5 mL of aqueous phase containing RE (III) and 5 mL of organic phase containing the extractant were mixed and shaken for 1 hour at 200 rpm using a mechanical shaker, which was sufficient for equilibrium. The mixtures were then centrifuged for 5 min at 8000 rpm to enhance the separation between aqueous and organic layers. The distribution coefficient of the ions in the aqueous and organic phase was expressed by the (1)

$$D = [S_{(\text{organic})}] / [S_{(\text{aqueous})}] \quad (1)$$

where the  $[S_{(\text{organic})}]$  and  $[S_{(\text{aqueous})}]$  are the concentration of the RE (III) in the organic and aqueous phase, respectively.

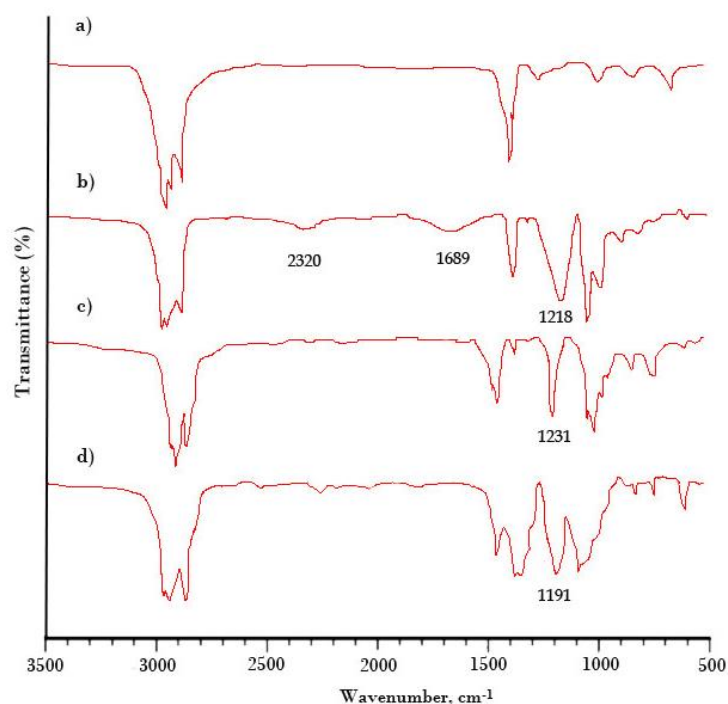
## RESULTS AND DISCUSSION

### *Interaction and Extraction Mechanism of [A336][DEHPA]:*

The interaction between DEHPA, A336 towards Sm were investigated by analysing the FTIR spectra of the extractants (individual extractants and synthesized bifunctional IL), before and after the extraction of Sm. Understanding the interaction between extractant and metals is crucial as it is the reflection of their efficiencies. As an example, various paper in the past has concluded that the abilities of DEHPA to extract metals are suppressed to the considerable extent due to the formation of dimer from the intermolecular hydrogen bonds (Cocalia *et al.*, 2005). Conjointly, hydrogen ions from the DEHPA also released by the ion-exchange mechanism, which increases the acidity of the system and thus, affects the metal extraction processes. In industrial approach, the commonly used method to overcome this phenomenon is by saponification process, which is neutralizing the system with ammonia solution. In the saponification process, DEHPA and ammonia

are converted into ammonium salt and once all the acidic extractant are removed the dimer will be broken. However, the saponification process resulted in a serious water pollution. Furthermore, addition of ammonium in the system is proven to reduce the ability of DEHPA to extract metals due to the formation of the third layer in the system and eventually the complete breakage of hydrogen dimer is not achieved (Zhao *et. al.*, 2016).

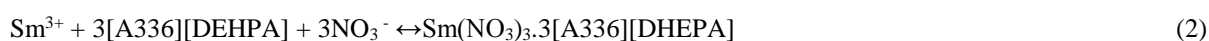
The IR spectra of A336, DEHPA, [A336][DEHPA] and Sm-[A336][DEHPA] along with their frequencies are presented in Fig. 1. The peak of the hydrogen bond dimer is shown in Figure 1b (DEHPA) at 1689  $\text{cm}^{-1}$  and the peak is completely disappeared in spectra c) ([A336][DEHPA]). The disappearance of the peak evidently indicates that the synthesized eliminates the formation of dimer and fully utilized the extraction capability of P=O group which depicted in spectra c) at 1231  $\text{cm}^{-1}$ . The shifting of the P=O peaks from 1231  $\text{cm}^{-1}$  in [A336][DEHPA] to 1191  $\text{cm}^{-1}$  in Sm-[A336][DEHPA] clearly indicates that P=O involved in the coordination reaction of the extraction system.

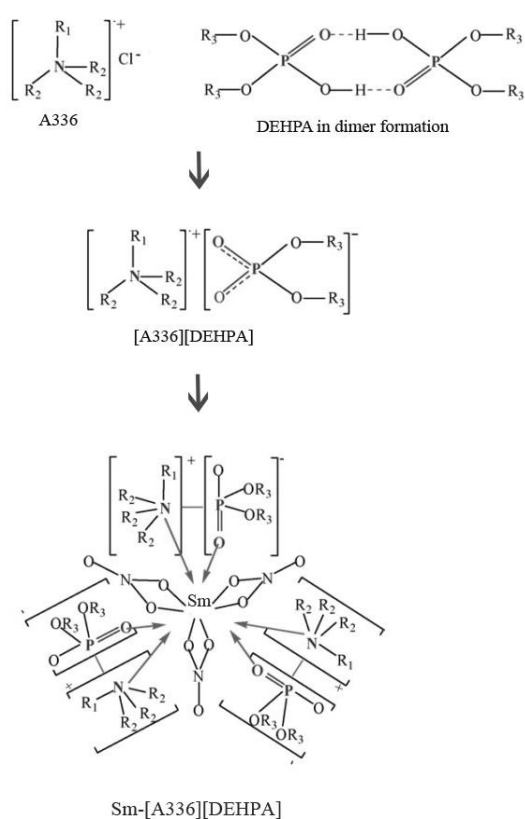


**Fig. 1:** IR spectra of a) A336 b) DEHPA c) [A336][DEHPA] d) Sm-[A336][DEHPA]

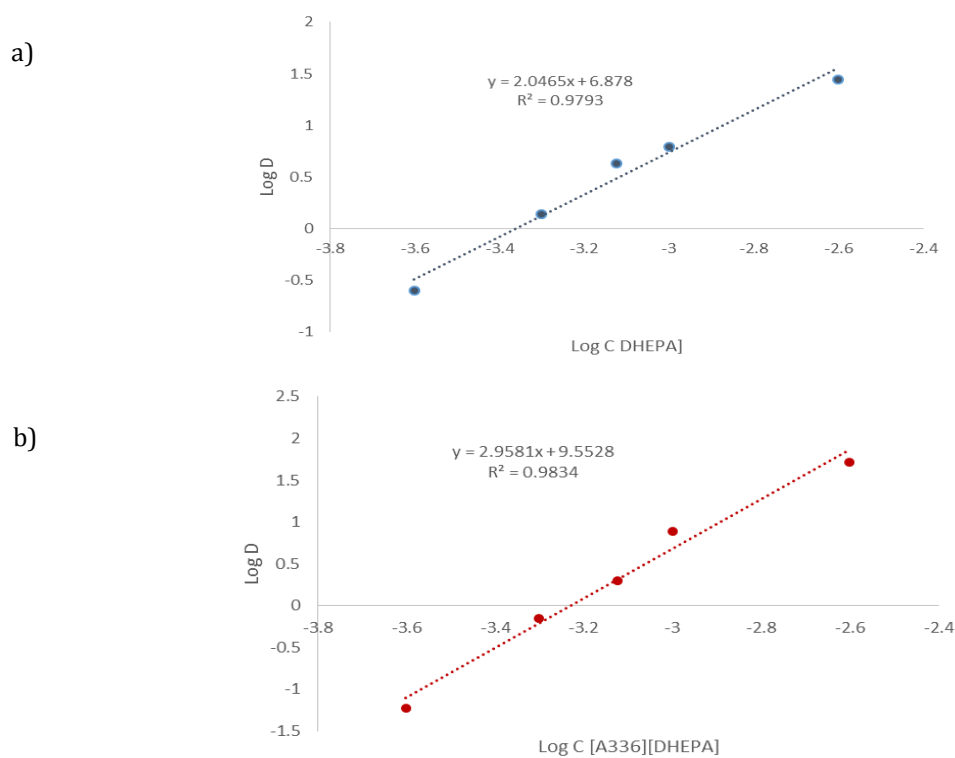
Aside from the capability of removing the dimer formation by the [A336][DEHPA], the synthesized bifunctional ionic liquid also provides better stability as well as stronger hydrophobicity feature in which lead to higher extraction efficiency compared to the individual extractants. The shifting of P=O band from 1218  $\text{cm}^{-1}$  in P204 to 1231  $\text{cm}^{-1}$  in [A336][DEHPA] proved that there is strong interaction between [A336] and [DEHPA] that able to improve the stability of the complex such as electrostatic, Van der Waals and induction interaction (Zahn *et al.*, 2008).

Extraction mechanism of Sm-[A336][DEHPA] system can be demonstrated using conventional slope analysis method. Figure 3 showed the plots of log distribution coefficient against log concentration of extractant. The plots give straight lines with the slope about 2 when using DEHPA as an extractant and almost 3 for [A336][DEHPA] when the extractant concentration was changed from  $2.5 \times 10^{-4}$  to  $5.0 \times 10^{-3}$  mol/L. In accordance with Danesi *et al.* (1970) in his report on slope analysis, the slope represent number of extractant molecules involved with the targeted metal in particular extraction system. For Sm extraction using DEHPA, 2 molecules of DEHPA interact with Sm and for the extraction using the IL, 3 molecules of [A336][DEHPA] needed for each Sm ion. Based on electroneutrality theory, neutral extractant ( $[\text{A336}]^+[\text{DEHPA}]^-$ ) will extract the cation (Sm (III)) and the anion ( $(\text{NO}_3)^-$ ) will be coextracted back into the system due to the electroneutrality. The proposed mechanism coordination for Sm-[A336][DEHPA] is illustrated in Figure 2 as previously reported by Sun *et al.* (2010b) for Eu (III). Accordingly, the mechanism of Sm-[A336][DEHPA] indicated to be ion association and the equation equilibrium and mechanism scheme as shown in :





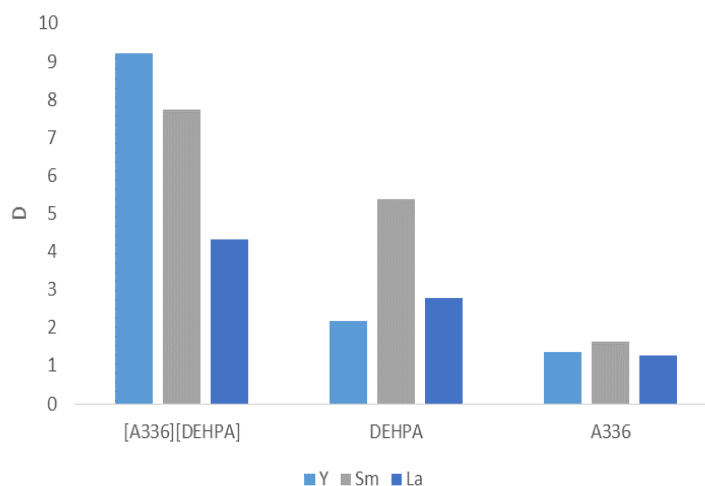
**Fig. 2:** The proposed mechanism and coordination of Sm-[A336][DEHPA]



**Fig. 3:** The effect of a) DEHPA and b) [A336][DEHPA] concentration on Sm (III) extraction in cyclohexane. Sm (III) =  $5.0 \times 10^{-4}$  mol/L at pH 4.3

### Synergistic Effect of [A336][DEHPA]:

Figure 4 shows the variation in distribution coefficient,  $D$  of La (III), Sm (III) and Y (III) in a solution of [A336][DEHPA] and their precursors. Each rare earth metals selected in this study are the representative of each rare earth group; La for light rare earth (LRE), Sm for medium rare earth (MRE) and Y for heavy rare earth (HRE). The distribution coefficient for all three rare earth ions are obviously higher in the [A336][DEHPA] than those of their precursor. The highest  $D$  was for Y (III) and followed by Sm (III) and La (III). Thus, the results indicate the potential use of the [A336][DEHPA] in extracting rare earth especially the one from the heavy group.



**Fig. 4:** The distribution coefficient of La (III), Sm (III) and Y (III) in [A336][DEHPA] and their precursors. RE (III) =  $5.0 \times 10^{-4}$  mol/L at pH 4.3

The synergistic enhancement factor,  $R$ , was determined using **Error! Reference source not found.** and presented in Table 1. Synergistic enhancement determines whether the binary extraction system creates synergism or antagonism. If  $R > 1$  means synergistic extraction occur whereas  $R < 1$  means antagonism. The results indicate that synergistic reaction takes place at all three ions with Y been the highest and the synergistic effect is increase with increasing ionic radii of the rare earth.

$$R = D_{[A336][DEHPA]} / (D_{[DEHPA]} + D_{[A336]}) \quad (2)$$

**Table 1:** Synergistic enhancement coefficient of La (III), Sm (III) and Y (III) in [A336][DEHPA] system

Rare earth ion	Synergistic Enhancement, R
Y (III)	2.62
Sm (III)	1.10
La (III)	1.06

### Conclusions:

The binary extractant system containing [A336][DEHPA] and their precursors have been used to study the interaction, mechanism as well as the inner synergistic effect of the system. Taking Sm ions as the representative of rare earth in the interaction and mechanism study, the mechanism is verified as ion association for [A336][DEHPAA] system. The [A336][DEHPA] also exhibits a prominent synergistic effect especially for HRE followed by MRE and LRE. The present study able to aid other researchers in selecting the appropriate extractant. However, an extensive study on the optimized extraction condition for rare earth containing minerals should be carried out. Such studies are underway in this laboratory.

### ACKNOWLEDGEMENT

This project is supported by Ministry of Higher Education Malaysia, RDU140141 as well as Internal Grant of Universiti Malaysia Pahang RDU 140339 and RDU 140369.

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