Hydrometallurgy 169 (2017) 306–313

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

# Solvent extraction of rare earths using a bifunctional ionic liquid. Part 1: Interaction with acidic solutions

James E. Quinn [a,*], Karin H. Soldenhoff [a], Geoffrey W. Stevens [b]

[a] *Australian Nuclear Science & Technology Organisation, Australia*
[b] *Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia*

ARTICLE INFO

*Article history:*
Received 9 August 2016
Received in revised form 21 January 2017
Accepted 12 February 2017
Available online 14 February 2017

ABSTRACT

Bifunctional ionic liquid extractants have been examined in recent years for the separation of rare earth elements by solvent extraction. One such extractant is the quaternary ammonium phosphonate ionic liquid '$R_4N^+EHEHP^-$' formed from Aliquat 336 (trioctyl/decylmethylammonium chloride) and EHEHPA (2-ethylhexyl phosphonic acid 2-ethylhexyl ester, also known as P507 or PC88A).

In this work, the uptake of hydrochloric acid by $R_4N^+EHEHP^-$ is investigated, by studying the effect of pH, chloride, diluent and extractant concentration and composition on the extraction of acid. A fundamental understanding of the interactions between $R_4N^+EHEHP^-$ and acid is considered crucial in order to describe the distribution of rare earths in such a system.

The results show that when dissolved in low concentration in a polar phase, the acid uptake by the ionic liquid as a function of pH is indistinguishable from EHEHPA. However, when dissolved in toluene at process relevant concentrations (up to 0.5 M), the protonation reaction occurs over a broader pH range and shifts to lower pH when compared with EHEHPA alone. Increasing the chloride concentration shifts the reaction to higher pH. The reaction stoichiometry, $^{31}P\{^1H\}$ NMR spectra and observed trends are consistent with protonation of the phosphonate ion and simultaneous formation of $R_4N^+Cl^-$. It is suggested that ion-pairing between the quaternary ammonium and phosphonate ions is responsible for the observed change in the protonation behaviour compared with EHEHPA alone. Our results indicate that the combination of Aliquat 336 and EHEHPA behaves as a mixture of $R_4N^+EHEHP^-$ and $R_4N^+Cl^- +$ EHEHPA, with the protonation dependent on the pH, and not as a different chemical form. Hence, regardless of how the ionic liquid has been prepared, once it is exposed to acid containing solutions, the acid-base behaviour of the ionic liquid is indistinguishable from a mixture of the two reagents.

## 1. Introduction

Industrial solvent extraction circuits used for the recovery and/or separation of metal ions utilise an active component (the extractant) dissolved in an inert and water immiscible organic solvent (the diluent). The relatively high volatility of most commonly used diluents can be of concern from an environmental standpoint. Room Temperature Ionic Liquids (RTILs) are entirely ionic compounds that are liquid at or below room temperature. They usually consist of bulky organic cations (e.g. tetraalkylammonium, imidazolium etc.) and organic or inorganic anions (e.g. hexafluorophosphate, tetrafluoro borate and chloride) (Han and Armstrong, 2007). RTILs have received some attention in recent years in a number of applications, including as a solvent in organic synthesis, in catalysis and in separation processes (Marsh et al., 2004). Apart from the interesting solvation chemistry often exhibited by this class of compound, they have also been suggested as an example of a so-called 'green' solvent. They are considered 'green' primarily due to their negligibly low volatility and generally high chemical stability (Zhao et al., 2005).

RTILs have been examined for the solvent extraction of metal ions, either as a replacement for conventional diluents or extractants, or used neat as both the extractant and the diluent (Dietz, 2006). Most RTILs, however, are considerably viscous at the near ambient temperatures relevant to industrial solvent extraction circuits (Marsh et al., 2004). Because of this, they would need to be dissolved into a suitable organic diluent for industrial applications, in much the same way that traditional extractants generally are. In fact, Aliquat 336 (trioctyl/decylmethylammonium chloride) is one such ionic liquid that, as early as the 1960s, has been examined or used industrially for metal extractions including Mo, V, Th, W, Zn and the rare earths (REs) (Ritcey, 2006). It is therefore important to note that there are no inherent environmental improvements offered by diluted RTILs as a class for solvent extraction, as a volatile diluent will still be required. Any environmental benefits would be achieved through either the lower toxicity, higher stability or lower aqueous solubility of the specific ionic liquid, or by a change in process chemistry that results in a more efficient separation and hence lower reagent consumption or production of waste solutions.

---

* Corresponding author at: Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.
*E-mail address:* jamesq@ansto.gov.au (J.E. Quinn).

http://dx.doi.org/10.1016/j.hydromet.2017.02.008
0304-386X/

Recently, bifunctional ionic liquid extractants (Bif-ILEs), also sometimes referred to as 'binary extractants' and 'acid base coupled (ABC) extractants', have been suggested for rare earth separations (Belova et al., 2009; Chen et al., 2013; Kalyakin and Kuz'min, 2000; Rout et al., 2012; Sun et al., 2010a; Sun et al., 2010b; Yang et al., 2016; Yang et al., 2012). The premise of a Bif-ILE is that both the cation and anion participate in the extraction mechanism. One example of this is an ionic liquid containing the quaternary ammonium cation from Aliquat 336 and the phosphonate anion from EHEHPA (2-ethylhexyl phosphonic acid 2-ethylhexyl mono ester, also known by trade names P507, PC 88A and Ionquest 801). Several claims have been made concerning improved separation factors achieved between certain rare earth ions (Chen et al., 2013; Sun et al., 2010a; Yang et al., 2016). This Bif-ILE extractant, henceforth referred to as '$R_4N^+EHEHP^-$', is the focus of the present study.

Understanding the behaviour of the Bif-ILE extractant in equilibrium with hydrochloric acid (HCl) solutions is a critical aspect of the study of rare earth extractions. Chen et al. (2013) attributed the decrease in RE distribution ratios with decreasing pH to competition for $R_4N^+EHEHP^-$ with the extraction of acid. They suggested that the mechanism of acid extraction is most similar to that of solvating extractants such as tributyl phosphate (TBP) or tri-*n*-octylphosphine oxide (TOPO) (Eq. (1)).

$$\overline{R_4N^+EHEHP^-} + HCl \rightleftharpoons \overline{(R_4N^+EHEHP^-)\cdot HCl} \tag{1}$$

The extraction of acid by ABC extractants was summarised by Eyal (1997). His analysis focussed on mixtures of amines with organic acids, including results for quaternary ammonium ions. While a number of different interactions were noted to be possible for these systems, the dominant reaction for extraction of strong mineral acids by quaternary ammonium ions at moderate acidities was one of conversion to the protonated acid/ammonium chloride forms as represented by Eq. (2) (where HA denotes the organic acid).

$$\overline{R_4N^+EHEHP^-} + H^+ + Cl^- \rightleftharpoons \overline{R_4N^+Cl^-} + \overline{HA} \tag{2}$$

Rout et al. (2012) suggest that the reaction for the mixture of Aliquat 336 and the closely related DEHPA (di-2-ethylhexyl phosphonic acid) is best represented by Eq. (2), although the researchers noted that the extent to which the reaction was occurring was not known. Belova and Khol'kin (2015) have also examined the extraction of acids with this type of extractant. They investigated the extraction of HCl by a mixture of Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) and Aliquat 336 and suggested that Eq. (2) was the more appropriate extraction mechanism.

Clearly, in order to draw any meaningful conclusions from the study of the extraction of RE with Bif-ILE, the interactions of the extractant with HCl/NaCl solutions needs to be better understood. The question that this study addresses is: In the context of RE extraction with $R_4N^+$-$EHEHP^-$ at extractant and acid concentrations relevant to industrial processes, does the reagent act as an undissociated ionic liquid throughout, or are the extractant properties reflective of the individual components? Part 1 of this study focuses on the extractant/acid interactions and Part 2 focuses on the extraction of rare earths. We chose to examine HCl as this is the most commonly used acid for rare earth separations (Liao et al., 2013).

## 2. Materials and methods

### 2.1. Materials

Aliquat 336 (methyltrioctyl/decylammonium chloride, >90% quaternary ammonium content, BASF) was used without purification. Ionquest 801 (2-ethylhexyl phosphonic acid 2-ethylhexyl mono ester, EHEHPA) was supplied by SNF FloMin and also not purified. The diluent in all experiments was toluene (Merck, >99.9% purity), although preliminary experiments revealed that aliphatic diluents would also be suitable. Toluene was selected because the sodium salt of EHEHPA does not form a third phase in this diluent, which simplifies comparisons between EHEHPA and $R_4N^+EHEHP^-$. The exception was one set of results in Section 3.3, for which Shellsol 2046 (narrow cut kerosene containing 17% aromatics, supplied by Shell) was used as diluent. Shellsol 2046 was used in this test to determine whether there were any significant differences when between toluene and a diluent more appropriate for industrial applications. All other reagents were of analytical grade.

### 2.2. Synthesis of ionic liquid

The ionic liquid $R_4N^+EHEHP^-$ was prepared using a modification of the method outlined by Sun et al. (2010b). Aliquat 336 chloride (482 g, 0.96 mol) was made up to 2 L in isopropanol and added to 1 L of 0.96 M KOH in isopropanol. A white precipitate of KCl formed immediately. After mixing at 50 °C for 4 h, the precipitate was removed by centrifuging using an Eppendorf Centrifuge 5810 at 3750 RPM, and the solution was diluted to 5 L using deionised $H_2O$. To this solution, 246 g of EHEHPA (0.79 mol) was added and refluxed at 50 °C for 12 h. After mixing was stopped, the upper layer was washed several times with deionised water to remove excess $R_4N^+OH^-$, then the excess isopropanol/water solvent was removed by using a Heidolph Hei-Vap rotary evaporator (50 °C/10 mbar) to yield a viscous orange liquid.

### 2.3. Extraction of acid and chloride (Section 3.1)

A 0.25 M sample of the $R_4N^+EHEHP^-$ was contacted with various solutions of 1 M NaCl at different acidities (10 mL of each phase). After the contact, the aqueous pH was measured, and the concentration of acid extracted was determined by the difference between the feed and equilibrium acidities. The chloride concentration in the organic sample was determined by first back stripping the sample with 5 M nitric acid to remove the extracted chloride. The chloride concentration was then measured by titration with silver nitrate in the presence of potassium chromate (Mohr's method). The chemical shift of the major resonance in the $^{31}P\{^1H\}$ NMR spectrum of each organic sample was recorded. Spectra were acquired on a Bruker Avance DPX400 at 161.97 MHz. Samples were run neat with a coaxial insert containing 0.1 M $H_3PO_4$ in deuterated acetone for referencing and locking, as described by Marie et al. (2012).

### 2.4. Potentiometric titrations

#### 2.4.1. Polar phase (Section 3.2)

$1.5 \times 10^{-3}$ mol of $R_4N^+EHEHP^-$ was added to 100 mL of 75% ethanol in water and titrated using 1.0 M HCl. pH measurements were performed using a Metrohm 6.0232.100 probe and 631 meter. The relationship between the pH as measured by the electrode and the concentration of acid in solution was determined by titration of a blank ethanol/water solution. The curves were then modelled as a simple acid protonation reaction as described in the text with an allowance for the acid required for the pH change. The same procedure was used for EHEHPA, except that this extractant was titrated using 1.0 M NaOH (to pH 11) followed by 1.0 M HCl back to the starting pH.

#### 2.4.2. Two-phase titrations (Sections 3.3–3.5)

20 mL of organic phase was mixed in aqueous continuous mode with an equal volume of aqueous solution, with the compositions of both as described in the text. The ionic strength was fixed at 1.0 M (NaCl/HCl) except when examining the effect of the total chloride concentration. Titrations were then conducted using 5.2 M HCl as the titrant for protonation or 1.0 M NaOH for deprotonation. The pH in the aqueous continuous dispersion was monitored directly using the same probe as