

Extraction of Nd and Y Using a Bifunctional Ionic Liquid

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The use of bifunctional ionic liquids for rare earth separations has attracted considerable interest in recent years. In this study, the extraction of Nd and Y by one such extractant is examined. The ionic liquid $R_4N^+EHEP^-$ consists of the quaternary ammonium ion from Aliquat 336 (trioctyl/decylmethylammonium chloride) and the phosphonate ion from EHEHPA (2-ethylhexyl phosphonic acid 2-ethylhexyl mono ester). The interaction of the ionic liquid with acidic solutions, as well as the extraction of the rare earths is studied and complemented by $^{31}P\{^1H\}$ NMR and visible absorption spectroscopy. The results show that the extractant decomposes to a mixture of the protonated acid and quaternary ammonium chloride, with rare earths extracted through cation exchange by the phosphonic acid.

1. Introduction

The separation of the rare earth elements is a difficult task, most commonly achieved industrially by solvent extraction using EHEHPA (2-ethylhexyl phosphonic acid 2-ethylhexyl mono ester, also known by trade names P507, PC-88A and Ionquest 801). Recently, several reports have emerged of the use of ‘bifunctional ionic liquids’ (an ionic liquid containing a deprotonated cation exchanger and the cation from an anion exchanger) for rare earth separations [1-8]. There is debate about the exact mechanism for the extraction of rare earth elements, with some researchers pointing to neutral or solvating extraction mechanisms, and others suggesting cation exchange by the acidic component. Large separation factors for certain rare earth pairs have also been reported for some bifunctional ionic liquid extractants compared with traditional cation exchange reagents [2, 8]. This study investigates the process chemistry of one such extractant ‘ $R_4N^+EHEP^-$ ’, consisting of the quaternary ammonium cation of Aliquat 336 (trioctyl/decylmethylammonium chloride), and the phosphonate anion of EHEHPA. The work was conducted at process relevant conditions to determine whether the use of an ionic liquid such as $R_4N^+EHEP^-$ provides any advantages in practice when compared with EHEHPA.

2. Experimental

2.1 Reagents

Aliquat 336 (BASF), EHEHPA (SNF FloMin) and TOPO (trioctylphosphine oxide, Cytec) were used as received. Shellsol 2046 (Shell) was used as the diluent in all experiments except when

examining the interaction with acidic solutions (Section 3.1). In this case, toluene was used as the diluent to allow for comparisons with EHEHPA, which forms a third phase in Shellsol 2046 but not in toluene. Solutions of Nd and Y were prepared by dissolving the oxides (Nd_2O_3 and Y_2O_3 , 99%) in HCl and diluting as required into the working solutions. All other reagents (NaCl, HCl, NaOH, KOH, isopropanol) were analytical grade reagents.

2.2 Preparation of Ionic Liquid

The reagent was synthesised using a modification of the procedure described by Sun et al. [9]. Aliquat 336 Cl (0.96 mol) was first added to a solution of KOH (0.96 mol) in isopropanol to convert to the quaternary ammonium hydroxide and precipitate KCl. This solution was then added to EHEHPA (0.79 mol) and mixed at 50 °C to form the quaternary ammonium phosphonate. The upper layer, which contained the extractant, was washed several times with water to remove the excess quaternary ammonium hydroxide and the solvent removed by rotary evaporation at 50 °C / 10 mbar.

2.3 Two-phase Titrations

A two-phase titration of $\text{R}_4\text{N}^+\text{EHEHP}^-$ was conducted by contacting the extractant (0.25 M) with a 1 M NaCl solution in a stirred beaker and adjusting the pH using 5 M HCl. The aqueous:organic phase ratio A:O was 1:1 and the temperature 21 °C. The pH of the dispersion was monitored using a Metrohm 6.0232.100 probe and 631 meter. The acid extraction (n_{HCl}) was determined by the difference between the acid added and that required for the measured pH change (as determined by a blank experiment with no extractant). The same process was conducted for EHEHPA, except that in this case the titrant was 1 M NaOH, and the moles of caustic consumed was calculated (n_{NaOH}). The results for both extractants were plotted as % protonation, defined as per Equations 1 and 2 (where $n_{\text{R}_4\text{N}^+\text{EHEHP}^-}$ and n_{EHEHPA} are the moles of extractant present in the organic phase):

$$\% \text{ Protonation } (\text{R}_4\text{N}^+\text{EHEHP}^-) = 100 \times \left(\frac{n_{\text{HCl}}}{n_{\text{R}_4\text{N}^+\text{EHEHP}^-}} \right) \quad (1)$$

$$\% \text{ Protonation } (\text{EHEHPA}) = 100 \times \left(1 - \frac{n_{\text{NaOH}}}{n_{\text{EHEHPA}}} \right) \quad (2)$$

2.4 Distribution Experiments

The distribution of Nd and Y between aqueous and organic phases was examined by first pre-equilibrating the organic phase (0.05 – 0.5 M $\text{R}_4\text{N}^+\text{EHEHP}^-$) with 1 M NaCl, with the pH of the dispersion controlled to the desired set point using 5 M HCl. A sample of the solvent was then withdrawn and the process repeated for successive pH set points. Each organic sample was then contacted with an aqueous phase containing 0.5 – 2.6 mM rare earths in 1 M NaCl / HCl solution for 30 minutes at the laboratory temperature (21 °C), at the same pH that the organic phase had been pre-equilibrated with. This ensured that the ionic strength of the aqueous phase remained constant in the distribution experiments, as otherwise the ionic liquid would have extracted HCl. The equilibrium pH was determined after the experiment. The A:O was 1:1 in all tests.

After the experiment, the organic phase was centrifuged and then stripped at an A:O of 2:1 using 5 M HCl. The feed solution, equilibrium aqueous and organic strip solutions were analysed by

ICP-MS (Perkin-Elmer Elan 9000) to determine the concentrations of Nd and Y.

2.5 Spectroscopy

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 0.5 M EHEHPA and $\text{R}_4\text{N}^+\text{EHEHP}^-$ before and after loading with yttrium were recorded using a Bruker Avance DPX400. A coaxial insert containing 0.1 M H_3PO_4 in deuterated acetone was used for locking and referencing. Visible absorption spectra (560 – 620 nm) of 0.5 M EHEHPA and $\text{R}_4\text{N}^+\text{EHEHP}^-$ after loading with 21 – 23 mM Nd at pH 3 were recorded using a VWR UV-3100PC spectrophotometer. For comparison, the spectrum of 0.25 M TOPO loaded with 0.035 M Nd was also analysed.

3. Results and Discussion

3.1 Protonation of Ionic Liquid

The titration results reveal that the ionic liquid exhibits quite distinct acid base behavior when compared with EHEHPA (Figure 1). EHEHPA deprotonates sharply at around pH 7, consistent with formation of the sodium salt (Equation 3). Some dissociation of the sodium salt to the aqueous phase is also possible. However, the aqueous phase solubility of the closely related DEHPA (di-2-ethylhexylphosphoric acid) in alkaline media at salt concentrations of 5 % was reported to be quite low at 55 ppm (0.17 mM) [10]. The ionic liquid is initially fully deprotonated, and extracts acid in a considerably broader reaction between pH 1 and 8, reaching an acid:extractant molar ratio of 1:1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the ionic liquid equilibrated at various pH values revealed a smooth downfield shift of the major resonance from 21.4 ppm (pH >8) to 30.2 ppm (pH <1). The NMR result is consistent with protonation of the phosphonate ion, and so it appears that Equation 4 is the appropriate expression for the extraction of acid by this extractant, that is protonation of phosphonate and formation of Aliquat 336-Cl as opposed to solvation of the acid (Equation 5).

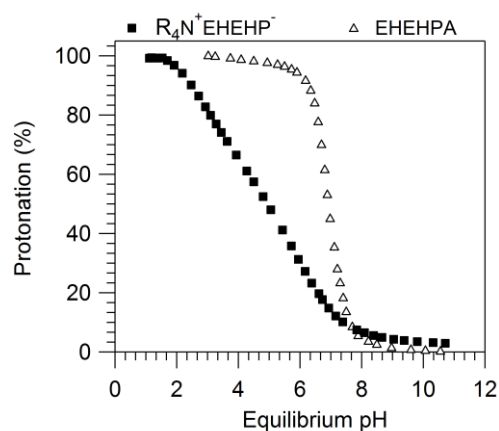
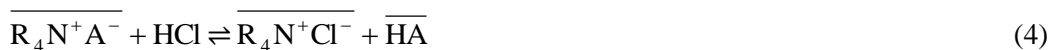
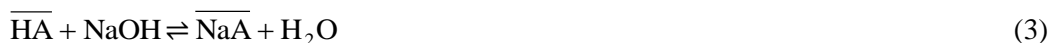


Figure 1. Protonation of 0.25 M extractants



The shift in protonation / deprotonation curve to lower pH, when compared with EHEHPA, is most likely to be due to ion pairing between the quaternary ammonium and phosphonate ions in the organic phase. The quaternary ammonium ion can be viewed as competing with protons for the available phosphonate ion. The change in acid-base behaviour means that the extractant is at least partially deprotonated in the expected region of interest for many rare earth separations (pH 1 – 5),

while for EHEHPA alone, the extractant remains almost fully protonated. The protonation reaction also has implications for recycling of the extractant after stripping with acidic solutions [11].

3.2 Extraction of Nd and Y

The effect of pH on the extraction of Nd and Y by $R_4N^+EHEHP^-$ is shown in Figure 2. The results show an increase in distribution ratios with increasing pH and extractant concentration. Yttrium is more strongly extracted than Nd, with a separation factor of around $\log \beta_{Y/Nd} = 3.2$. This is of a similar order as the literature separation factor for EHEHPA ($\log \beta_{Y/Nd} = 2.9$ [12]). The slope in the plot of $\log D$ vs pH ranged from around 1.6 to 1.8 for Nd (measured at $D=1$), with lower slopes measured at elevated pH (>3). For Y, measured between 0.1 and 1 M HCl, the slope was 2.6. Compared with data we have previously reported for 0.5 M EHEHPA under similar conditions, the extraction of yttrium by $R_4N^+EHEHP^-$ is weaker [13], meaning that it requires higher pH to achieve the same extraction.

The slope analysis indicates that at $pH < 1$, the results are similar to what is generally observed for cation exchange by acidic extractants such as EHEHPA: i.e. a slope of approximately three in a plot of $\log D$ vs. pH (Equation 6). At elevated pH, however, the slopes are lower than this and the lines are concave down, which is not typically observed for EHEHPA.



An acid dependency in the extraction of rare earth elements has been reported for bifunctional ionic liquid extractants such as $R_4N^+EHEHP^-$ [2-7, 14]. It has been attributed either to the cation exchange behavior of the phosphonate ion, or to a neutral extraction mechanism for extraction of rare earths that is impacted upon by the co-extraction of acid (also by a neutral mechanism). In order to resolve this question, spectroscopic studies were carried out (Section 3.3). It should be possible to distinguish spectroscopically between a cation exchange complex formed with EHEHPA (i.e. $RE(HA_2)_3$) and a neutral complex of the form $RECl_3 \cdot (R_4N^+EHEHP^-)_n$.

3.3 Spectroscopy of complexes

The visible absorption spectra of Nd loaded EHEHPA and $R_4N^+EHEHP^-$ are compared in Figure 3.

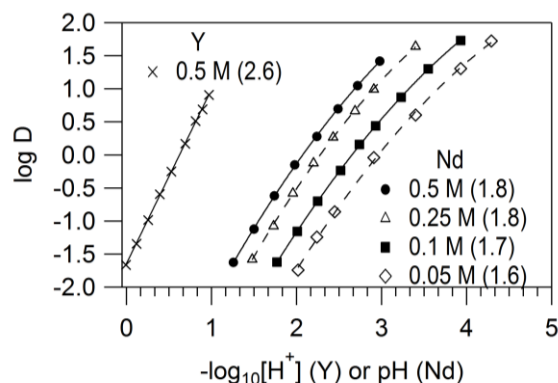


Figure 2. Effect of pH on extraction of Nd, Pr. ($R_4N^+EHEHP^-$ concentration as specified, slope of curve at pH_{50} in brackets)

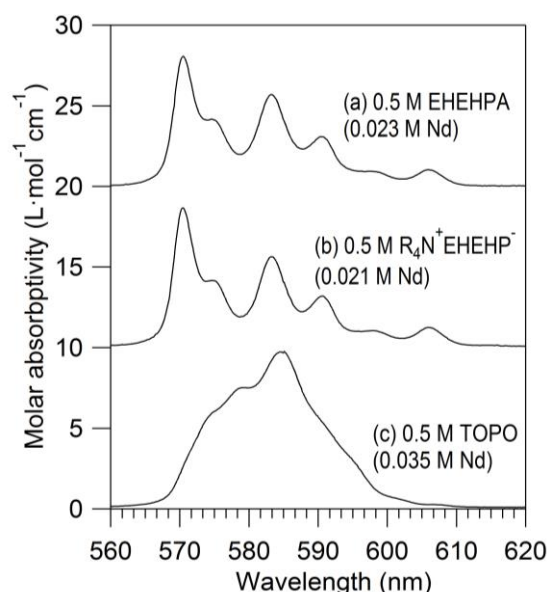


Figure 3. Visible absorption spectra of Nd loaded organic phases (spectra offset by $10 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)

The Nd^{3+} ion features a hypersensitive transition at around 570 nm. The spectrum for Nd loaded EHEHPA (Figure 3a) is similar to one previously reported, indicative of pseudo-octahedral geometry consistent with either $\text{Nd}(\text{HA}_2)_3$ or Nd_2A_6 [15]. Also shown in Figure 3c is the spectrum for a sample of Nd loaded TOPO (tri-n-octylphosphine oxide). The complex in this case would be of a $\text{NdCl}_3 \cdot (\text{TOPO})_n \cdot (\text{H}_2\text{O})_m$ adduct. The spectra are significantly different, with less well defined peaks with a maximum at approximately 585 nm in the Nd-TOPO spectrum. This is indicative of a change in coordination between the neutral complex compared with the cation exchange complex formed with EHEHPA. However, the spectrum for Nd loaded $\text{R}_4\text{N}^+\text{EHEHP}^-$ is indistinguishable from that of EHEHPA (Figure 3b).

$^{31}\text{P}\{^1\text{H}\}$ NMR was used to examine the chemical environment of the phosphorus containing ligands in EHEHPA and $\text{R}_4\text{N}^+\text{EHEHP}^-$. Spectra were recorded on neat samples of 0.5 M extractants before and after partially loading with yttrium (Figure 4). Yttrium was chosen in this case as Y^{3+} is diamagnetic and therefore there is no splitting of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The approach is based on a similar study using DEHPA and lanthanum [16]. The EHEHPA spectrum prior to loading with yttrium reveals a single major signal at 30.7 ppm, with several minor peaks indicative of impurities of the commercial grade samples. After loading with yttrium, an additional signal is observed at 23.4 ppm, with considerable line broadening. The new complex is presumably the phosphonic acid associated with the yttrium complex, and the broadening indicates exchange between the free and complexed phosphonic acid. For $\text{R}_4\text{N}^+\text{EHEHP}^-$, the spectrum prior to loading (but after pre-equilibrating the extractant to pH 2), reveals a signal at 26.0 ppm. After loading, two signals are observed at 25.1 and 23.3 ppm. The former, based on integration of the signals, is consistent with the un-complexed phosphonate / phosphonic acid. The latter is in exactly the same position as the Y-EHEHPA signal. This suggests that:

- 1) The chemical environment of the uncomplexed phosphonate / phosphonic acid is different from EHEHPA and changes with pH, consistent with results presented in Section 3.1, and
- 2) The chemical environment of the phosphonate ion complexed with yttrium is identical to that in the Y-EHEHPA complex.

3.4 Proposed Mechanism

The visible and NMR spectroscopy in Section 3.3 reveals that the chemical environment of the both the metal and ligand are identical for EHEHPA and $\text{R}_4\text{N}^+\text{EHEHP}^-$; in other words the complex formed is identical for the two extractants. However, the Nd and Y extraction data for $\text{R}_4\text{N}^+\text{EHEHP}^-$ (Section 3.2) is quite different from the cation exchange behavior of EHEHPA, with curved log D vs pH plots with slope <3 , with the magnitude of the slope being dependent on the equilibrium pH. In

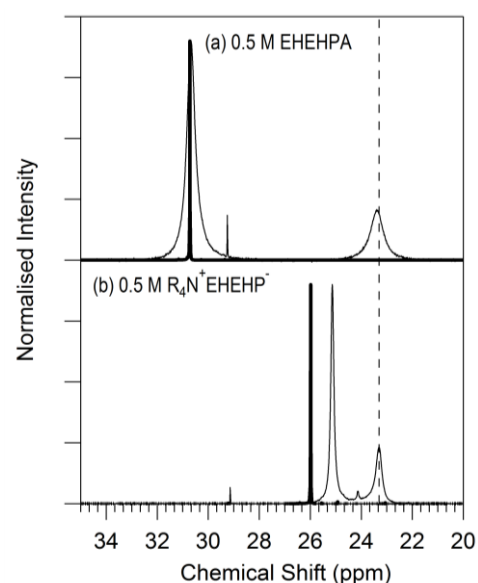


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of organic phases before and after loading with 26 mM Y (thick lines: prior to loading)

addition, the distribution ratios are depressed compared with EHEHPA alone.

Our hypothesis for this apparent discrepancy lies with the acid base behaviour evident in the results of Section 3.1. At low pH, the data indicates that the extractant is predominantly protonated, while as the pH increases the phosphonic acid is

increasingly deprotonated favouring formation of the ionic liquid. If it is assumed that the dominant extraction mechanism is one of cation exchange by the phosphonic acid (as evident in the spectroscopic data), then increasing the pH would on one hand favour the extraction of rare earths (Equation 6), but on the other hand the free phosphonic acid concentration would decrease, which would decrease the extraction of rare earths. The latter explains the reduced slopes and curved nature of the plots at elevated pH, as well as the antagonism compared with EHEHPA alone. The proposed mechanism represented in Figure 5 is consistent with the slope analysis and spectroscopy data obtained in this study.

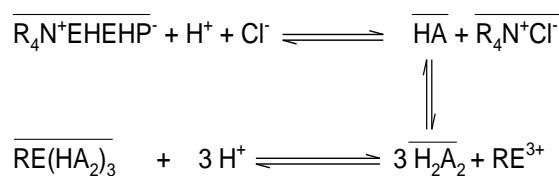


Figure 5. Proposed extraction mechanism

4. Conclusion

The results demonstrate that the ionic liquid extractant $\text{R}_4\text{N}^+\text{EHEHP}^-$ extracts acid and decomposes to a mixture of EHEHPA and $\text{R}_4\text{N}^+\text{Cl}^-$ after equilibration with HCl solutions. This has a pronounced effect on the extraction of rare earths, shifting the extraction to higher pH and lower slopes compared with EHEHPA. $^{31}\text{P}\{^1\text{H}\}$ NMR and visible absorption spectroscopy revealed that the extracted complex was identical to that formed upon extraction by EHEHPA. The proposed mechanism for the ionic liquid is one of extraction of rare earths through cation exchange by the phosphonic acid, moderated by the pH dependent interaction between the phosphonate and quaternary ammonium ions.

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