



Synthesis of novel nonsymmetric dialkylphosphinic acid extractants and studies on their extraction–separation performance for heavy rare earths



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ABSTRACT

The extraction and separation of heavy rare earths is always one of the most challenging unit operations in hydrometallurgy. Research and development of novel efficient extractant is one way to solve this problem. Organophosphinic acid is a good potential extractant. A new method was established for the synthesis of nonsymmetric dialkylphosphinic acid (NSDAPA) ($R'R''POOH$, $R' \neq R''$), optimized the synthesizing conditions of the key intermediate mono-alkylphosphinic acid and successfully synthesized three novel extractants (*n*-octyl)(2,4,4'-trimethylpentyl) phosphinic acid, (*n*-octyl)(cyclohexyl)phosphinic acid and (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid. The extraction ability of the novel extractants was investigated. The structure–property relationship and the separation performance for heavy rare earth couples Er/Y, Y/Ho, Yb/Tm and Lu/Yb were evaluated.

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1. Introduction

Acidic organophosphorus extractants are widely used in extraction and separation fields for actinide/lanthanide (Chen et al., 2011; Hill et al., 1998), rare earths (Hino et al., 1997; Wang et al., 2013; Shen et al., 1991) and Co/Ni (Li et al., 2010; Xing et al., 2012) etc. The extractants such as 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (EHEHPA, PC 88A or P507) and di-(2,4,4'-trimethylpentyl)-phosphinic acid (Cyanex 272) (see Table 1) are the most commonly used extractants in rare earth extraction and separation industry. However, they do not satisfy the increasing demands for high purity, environmental protection and energy conservation in production process. For P507, it requires high stripping acidity for heavy rare earths and its selectivity for Tm/Yb/Lu is poor. Although Cyanex 272 can remedy these shortages to a certain degree, the low extraction capacity, emulsion formation during extraction and high price limit its wide application. Its selectivity for some couples of rare earth elements (e.g. Gd/Eu, Er/Y, Lu/Yb) is still poor (Huang, 2003). To develop more efficient extractants for heavy rare earths, many scientists turned their focus on dialkylphosphinic acids (DAPAs) (Hino et al., 1997; Wang et al., 1997, 2013). We also designed and synthesized some DAPAs (R_2POOH) with different carbon-chain length and branched chain in different positions and studied their extraction and separation performance for Tm/Yb/Lu systematically. We found that the nearer the branched chain moved to P atom, the more reduction generated on the extraction ability and it descended down in the following sequence:

HYY-5 ($R = n$ -pentyl) \approx HYY-9 ($R = n$ -hexyl) $>$ P507 $>$ HYY-2 ($R = 2,3$ -dimethylbutyl) $>$ HYY-11 ($R =$ cyclohexyl) $>$ HYY-1 ($R = 2,4,4'$ -trimethylpentyl) $>$ HYY-8 ($R = 1$ -methylbutyl) (Wang et al., 2013). Among these extractants, the extraction ability of new compound HYY-2 fell in between P507 and Cyanex 272. It possessed higher extraction capacity than Cyanex 272 and lower stripping acidity compared with P507. Besides, it exhibited better separation performance for heavy rare earths Tm/Yb/Lu at pH 2.00. However, there might be drawbacks such as relatively large solubility in an aqueous phase caused by the low number of carbon atoms (or shorter carbon chains). For DAPA, its structure was not diverse owing to the limit of olefins' structure.

Steric hindrance and electronic effect of nonsymmetric dialkylphosphinic acid (NSDAPA, $R'R''POOH$, $R' \neq R''$) can be fine-tuned by changing both of its alkyl structures and thus changing its extraction and separation performance. So NSDAPA can open the door to exploration of a number of potential separation systems with this class of extractants. Combining two DAPA structures, of which one with strong extraction ability (such as HYY-5 & HYY-9) and another one with weak extraction ability (like HYY-1), might generate an excellent novel extractant of which extraction ability fall in these two DAPAs. Besides, considering the solubility of NSDAPA in the aqueous phase, its carbon atoms could not be too less, and the linear alkyl we chose was *n*-octyl. So the NSDAPA structures we designed were as follows: (*n*-octyl)(2,4,4'-trimethylpentyl)phosphinic acid (structure combination of HYY-1 & di-*n*-octylphosphinic acid similar to HYY-9), (*n*-octyl)(cyclohexyl)phosphinic acid (structure combination of HYY-11 & also di-*n*-octylphosphinic acid) and (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid (structure combination of HYY-1 &

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Table 1

Names, molecular formula, structural formula and molar mass of extractants.

No.	Name	Molecular formula	Structural formula	Molar mass (g/mol)
P507	2-Ethylhexylphosphoric acid Mono-2-ethylhexyl ester	C ₁₆ H ₃₅ PO ₃		306.43
Cyanex 272	Di-(2,4,4'-trimethylpentyl)-phosphinic acid	C ₁₆ H ₃₅ PO ₂		290.42
HHY-2	Di-(2,3-dimethylbutyl) phosphinic acid	C ₁₂ H ₂₇ PO ₂		234.32
HHY-9	Di-(n-hexyl)phosphinic acid	C ₁₂ H ₂₇ PO ₂		234.32
5a	(n-Octyl)(2,4,4'-trimethylpentyl) phosphinic acid	C ₁₆ H ₃₅ PO ₂		290.42
5b	(n-Octyl)(cyclohexyl)phosphinic acid	C ₁₄ H ₂₉ PO ₂		260.35
5c	(2,3-Dimethylbutyl) (2,4,4'-trimethylpentyl)phosphinic acid	C ₁₄ H ₃₁ PO ₂		262.37

HHY-2) (see Table 1), which have been reported previously in our patent (Xu et al., 2014).

Reports about the synthesis of NSDAPA are few and till now only some patents referred to this. For example, Robertson (1982) reported the synthetic method of (2,4,4'-trimethylpentyl)(cyclohexyl)phosphinic acid and its performance for Co/Ni separation; and Zhou et al. (2007) reported the synthesis of (2,4,4'-trimethylpentyl)(2,2',4,4'-tetramethylbutyl) phosphinic acid and its sulfur derivatives. In these reports, the phosphorus source was PH₃. It was reacted with one olefin at a certain temperature and pressure through free radical addition reaction to yield mono-substituted phosphine (R'PH₂), then reacted with another olefin to yield nonsymmetric di-substituted phosphine (R'R''PH, R' ≠ R'') which was then oxidized to NSDAPA by H₂O₂ (Scheme 1(a)). This method has several shortcomings, such as PH₃ is highly toxic gas; the reaction requires high pressure and is difficult to control; and removal of the byproducts is another difficulty. In the process of R'PH₂ synthesis, di- and tri-substituted phosphines (R'₂PH & R'₃P) could be inevitably formed. Similarly in the synthesis process of R'R''PH, it is also inevitable to generate tri-substituted phosphine R'R''₂P. All these byproducts are difficult to remove. Besides, in the oxidation process of R'R''PH to R'R''POOH, the temperature control is very important. Higher temperature tends to remove one alkyl group forming some mono-alkylphosphonic acid and lower temperature slows the reaction and causes excessive reaction time (Robertson, 1982; Rickelton et al., 1982). So it is difficult to obtain the pure NSDAPA product and this restrains its research and application.

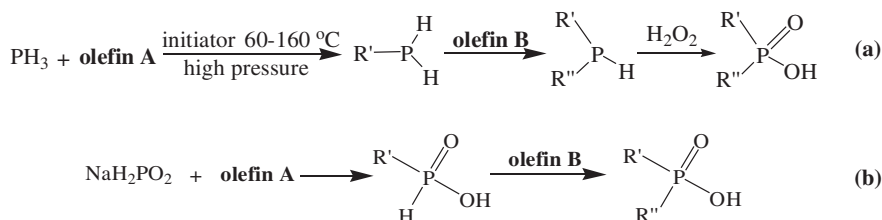
In this paper, we chose sodium hypophosphite as the phosphorus source. It was first reacted with one olefin to yield monoalkylphosphinic acid (MAPA), and then reacted with another olefin to yield NSDAPA (Scheme 1(b)). As the MAPA synthesis and purification are the keys, its synthetic conditions were explored and optimized and the purification methods were discussed. The extraction performances of synthesized NSDAPAs for heavy rare earths Ho, Er, Tm, Yb and Lu were investigated and compared with Cyanex 272, P507 and DAPAs with the same alkyl structure as one of the alkyl groups of NSDAPAs. The effect of alkyl structure on NSDAPA extraction ability was revealed. Their separation performance for heavy rare earth couples Er/Y, Y/Ho, Yb/Tm and Lu/Yb was determined.

2. Experimental

2.1. Reagents

Sodium hypophosphite, acetic acid, cyclohexane, tetrahydrofuran, and 1,4-dioxane were of analytical reagent (A.R.). *n*-Octane used as a reaction solvent and extractant diluent, and di-*tert*-butyl peroxide and azo-*iso*-butyronitrile used as an initiator were all of chemical purity (C.P.).

Diisobutylene provided by Zibo Runfu Chemical Technology Co., Ltd was composed of 76% 2,4,4-trimethyl-1-pentene and 20% 2,4,4-trimethyl-2-pentene. 2,3-Dimethyl-1-butene was provided by Dalian



Scheme 1. Synthetic route of NSDAPAs.

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