

Extraction of Eu-152, Nd and Am-241 from the Simulated Liquid Wastes by Picolinamide(C₈H₁₇)

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Abstract

Trivalent actinide-lanthanide group separation is difficult to perform on an industrial scale, because of the many drawbacks of the available chemical process. In this paper, picolinamide(C₈H₁₇) is synthesized and characterized, and extraction yields of Am-241, Eu-152 and Nd are determined in batch extraction experiments. In particular, the influence of the solvent is described. The extraction yields of Am-241, Eu-152 and Nd depended on the LiNO₃ concentration, the picolinamide(C₈H₁₇) concentration and the acidity. A favorable picolinamide(C₈H₁₇) concentration was found to be about 2M. The appropriate nitric acid concentration and LiNO₃ concentration were confirmed to be about 0.125M and 3M, respectively. The separation factor of Am and Eu was about 9.9 at optimum conditions. The picolinamide(C₈H₁₇) is a very promising extractant for the actinide(III)-lanthanides(III) separation.

Key Words : picolinamide, extraction, liquid waste, actinide, lanthanide

1. Introduction

Much attention has been paid to group partitioning and transmutation in developing technologies for peaceful uses of nuclear energy, to improve the disposal of HLLW (High Level Radioactive Liquid Waste) generated from the chemical treatment process of spent fuel, and to announce public information about its safe

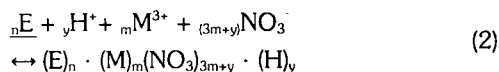
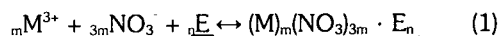
disposal [1,2]. HLLW is composed of MA (Minor Actinides), RE (Rare Earths), Cs & Sr, PGM (Platinum Group Metals), and FP (Fission Product). Group partitioning of the radionuclides is classified as MA, RE, Cs & Sr, PGM, and FP groups based on chemically similar properties. For this partitioning, ion-exchange, precipitation, crystallization, and solvent extraction have been widely studied. Presently, several separation

methods with respect to solvent extraction are in progress, e. g. TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous complexes) and reversed-TALSPEAK processes developed by the US, TRUEX (TRansUranium EXtraction) process for radioactive waste used in the army, CTH (Chalmers university of TecHnology) process investigated by Sweden, DIAMEX (DIAMide EXtraction) process of France, TRPO (TRialkyl Phosphine Oxide) process in China, DIDPA (Di-IsoDecyl Phosphoric Acid) process in Japan [3-7]. As a potential extractant for the solvent extraction, DEHPA (di(2-ethylhexyl) phosphoric acid), DIDPA, and O ϕ D(iB)CMPO (Octyl(phenyl)-N, N-diisobutyl carbamoylmethyl phosphine oxide) are usually being used but its industrial usage has not been applied yet [8,9].

With this in mind, we now report the synthesis of picolinamide(C₈H₁₇) as a soft-donor extractant able to play an important role in MA-RE mutual separation and investigation of the extraction characteristics of Nd, Eu-152, and Am-241 in batch system. The picolinamide(C₈H₁₇) was known to have a great extractability along with a decrease of the secondary waste through perfect combustion and usefulness in highly concentrated nitric acid medium in which the concomitant FP is not precipitated.

2. Theory

Picolinamide(C₈H₁₇) as a soft donor extractant, shows a potential selectivity toward actinide elements over lanthanides. The ligand reacts with the specific metal ion followed by transporting it from an aqueous phase into an organic phase as indicated in the equations (1) and (2) in the absence and presence of nitric acid medium, respectively. However, the detail transporting mechanism is not reported so far [12].



where underlined expression indicates organic phase, M for trivalent metal ion, E for picolinamide(C₈H₁₇). m, n, and y are able to be influenced by medium species and diluents but adequate values were not given yet. The distribution constant and separation factor are defined by $D_M = (\text{metal concentration in organic phase}) / (\text{remaining metal concentration in aqueous phase})$ and $SF_{A/B} = D_A / D_B$, respectively.

3. Synthesis of Picolinamide(C₈H₁₇)

Picolinamide(C₈H₁₇) was prepared from adaptation of the reported method performed by Cuillardier and Musikas [10, 12]. Under nitrogen conditions, to a solution of picolinic acid (5.0 g) dissolved in benzene (50 ml), oxalyl chloride (17.3 ml) was added dropwise during a period of 1 hour at 70°C. One drop of pyridine was added and then the color of the reaction mixture changed into yellow. The reaction mixture was allowed to reflux for 4-5 hours. After cooling down to room temperature, removal of the solvent used *in vacuo* to give a black solid which corresponds to picolyl chloride. To this reaction, a methylene chloride (100 ml) and triethylamine (5.38 ml) was slowly added under ice bath. Stirring for 2-3 hours at room temperature gave a deep brown mixture. 10% NaHCO₃ (100 ml) was added and the organic layer was separated. The organic phase was washed with water (100 ml \times 2) and dried over anhydrous magnesium sulfate. Magnesium sulfate was filtered and the solvent was removed *in vacuo* to give a brownish oil. Purification using column chromatography with ethyl acetate and hexane as eluent on silica gel, provided a pale yellow oil with

79 % of yield. This final product was approved by IR, NMR, and Mass spectroscopic data.

4. Experimental and Analysis

Picolinamide(C_8H_{17}) as an extractant, benzene or carbon tetrachloride as a diluent, and $LiNO_3$ or HDNNS ($HO_3SC_{10}H_5(C_9H_{19})_2$) as an additive were used. Trace amounts of Am-241 and Eu-152 for MA and RE, respectively were used. 0.0434M Nd considered as an actual concentration were possibly contained in the radioactive waste was used. The HDNNS was obtained from Alfa. The Am-241 and Eu-152 were purchased from Isotope Product Laboratories. Other chemicals in this experimental were used as received from the Aldrich chemical company without any further purification. All the liquid-liquid extractions were performed in 16 ml vials ; equal volumes of organic and aqueous phases were contacted automatically by an end-over-end rotation for 5 minutes at 23 ± 1 °C. One day after the aqueous and organic phases were sampled, and analyzed by the use of Liquid Scintillation Analyzer (Packard Model : 2500 TR/AB) for radioactive isotope Am-241 and Eu-152. Nd was analyzed by using ICP (Inductively Coupled Plasma atomic emission spectroscopy : Jobin Yvon model JY 38 plus).

5. Results and Discussion

5.1. Effect of Picolinamide(C_8H_{17}) Concentration

Figure 1 indicates extraction yields of Nd, Eu-152, and Am-241 with changes of picolinamide (C_8H_{17}) concentration. Using the ligand having less than 1.0M concentration, only a little Am-241 was extracted, but little Nd and Eu-152 were extracted. By increasing the ligand concentration from 1.0M to 2.0M, the extraction yield of Am-

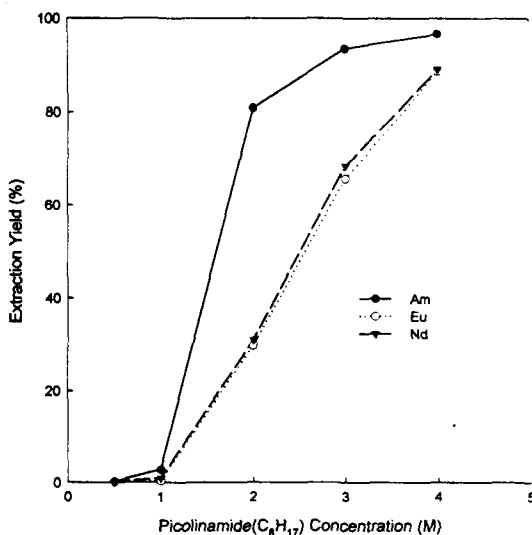


Fig. 1. Effect of Picolinamide(C_8H_{17}) Concentration on the Extraction Yield of Am, Eu and Nd at $[LiNO_3] = 3M$ and $[HNO_3] = 0.125M$

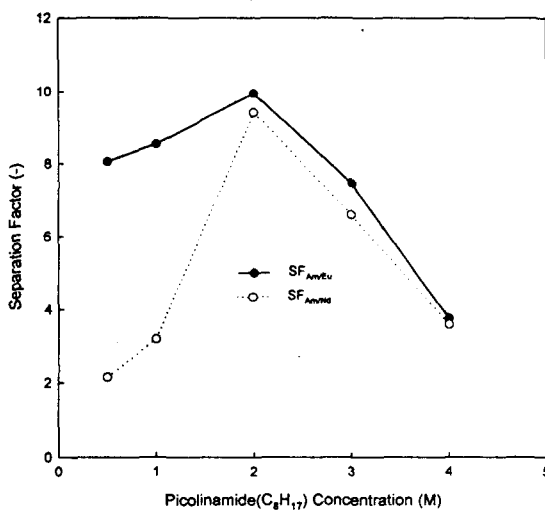


Fig. 2. Effect of Picolinamide(C_8H_{17}) Concentration on the Separation Factors($SF_{Am/Eu}$ and $SF_{Am/Nd}$) at $[LiNO_3] = 3M$ and $[HNO_3] = 0.125M$

241 remarkably increased, but gave a slow increment in the case above 2.0M ligand concentration. The extraction yield trend for Nd is similar to that for Eu-152. Both Nd and Eu-152

show straight increments in the range from 1.0M to 3.0M but becoming a smooth slope as compared with Am-241. Above 3.0M, the slope slowly increases. Figure 2 indicates separation factors for each of the metal ions. 2.0M picolinamide(C_8H_{17}) provided a good separation factor toward Am-241 over Eu-152 and Nd. With the above experimental results, we could conclude that a ligand concentration higher than 2.0M provides a low separation factor due to high extraction yields for all of Nd, Eu-152, and Am-241. In addition, in the case of relatively low concentration of the ligand, it is assumed to be difficult to separate by low extraction efficiency. Using 2.0M picolinamide (C_8H_{17}), 30.9%, 29.8%, and 80.8% of extraction yields for Nd, Eu-152, and Am-241 were obtained respectively. In this condition, a separation factor of 9.9 for Am-241 over Eu-152 was given as well, indicating a good separation efficiency. This is attributable to the fact that picolinamide(C_8H_{17}) bears the nitrogen donor which selectively responds to actinides over rare earth metal cations.

5.2. Effect of $LiNO_3$ and Nitric Acid Concentration

Extraction yield changes of Nd cation with nitric acid and lithium nitrate concentration are depicted in Figure 3. The Nd extraction yield gradually increases with $LiNO_3$ concentration and shows the maximum increment in the condition of 3.0M~5.0M $LiNO_3$. It is thought that as the $LiNO_3$ concentration increases, the nitrate concentration is also increased and then the concomitant Nd cation easily transports based on the equation (2). Nd extraction yield was not influenced by the nitric acid concentration in the case of less than 1.0M $LiNO_3$ whereas the extraction yield increases with nitric acid concentration from 1.0M to 3.0M concentration of $LiNO_3$. At over 3.0M $LiNO_3$, the

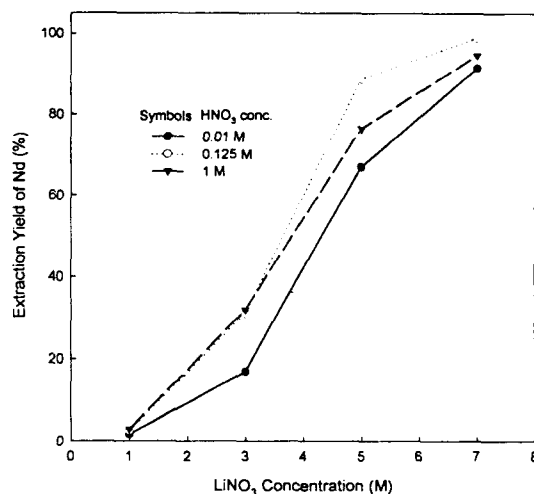


Fig. 3. Extraction Yield of Nd with Changes of $LiNO_3$ Concentration for Various HNO_3 Concentrations at $[Picolinamide(C_8H_{17})] = 2M$

maximized extraction yield for Nd was observed in 0.125M nitric acid medium. In the case of $LiNO_3$ concentration below 1.0M, the nitrate salt demanded in the equation (2) is too deficient to extract the Nd cation. Conversely, in the range from 1.0M to 3.0M, the nitrate anion of nitric acid is able to participate in the reaction, resulting in an increment of nitrate salt. It is anticipated that when the $LiNO_3$ concentration is over 3.0M for Nd extraction, nitrate salt from nitric acid and $LiNO_3$ are applicable to the equation (2). In addition, some part of nitrate salt is assumed to react with the ligand to bring a low extraction yield.

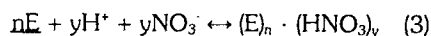


Figure 4 indicates the extraction yield of Eu-152 with $LiNO_3$ and nitric acid concentration. As increasing the $LiNO_3$ concentration, the extraction yield of Eu-152 remarkably increases for all of the nitric acid concentrations. In the case of over 5.0M of $LiNO_3$ concentration, the Eu-152 extraction yield slowly increases. In particular, the extraction yield of Eu-152 is influenced by $LiNO_3$

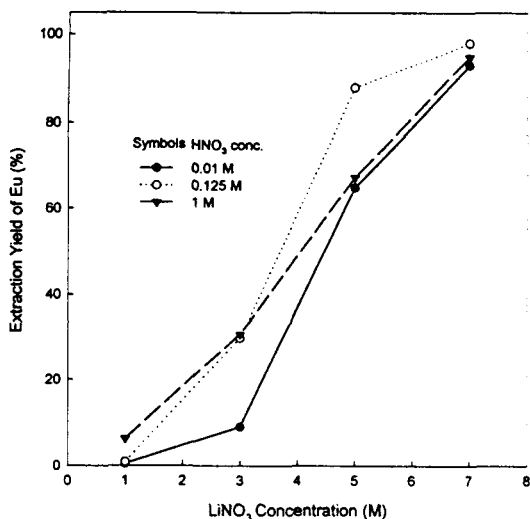


Fig. 4. Extraction Yield of Eu with Changes of LiNO₃ Concentration for Various HNO₃ Concentrations at [Picolinamide (C₈H₁₇)] = 2M

concentration. At below 3.0M of LiNO₃ concentration, the extraction yield of Eu-152 increases with nitric acid concentration. At over 3.0M of LiNO₃ concentration, the extraction yield of Eu-152 sharply increases but shows a maximum extraction yield in 0.125M nitric acid concentration. This propensity for Eu-152 and Nd concerning the extraction yield is assumed to have originated from chemically similar properties within a lanthanide series. Figure 5 indicates the extraction yield of Am-241 with LiNO₃ and nitric acid concentration. The extraction yield of the Am-241 increases more remarkably than that of Nd and Eu-152. This is probably explained by the increment of nitrate species coming from LiNO₃ which makes the equation (2) acceptable as well as excellent selectivity of picolinamide(C₈H₁₇) toward Am-241 over Nd and Eu-152. The extraction yield for Am-241 varies in direct proportion to nitric acid concentration in the case of LiNO₃ concentration below 2.0M. For over 2.0M LiNO₃, 0.125M concentration of nitric acid medium provided the optimum extraction yield. In both

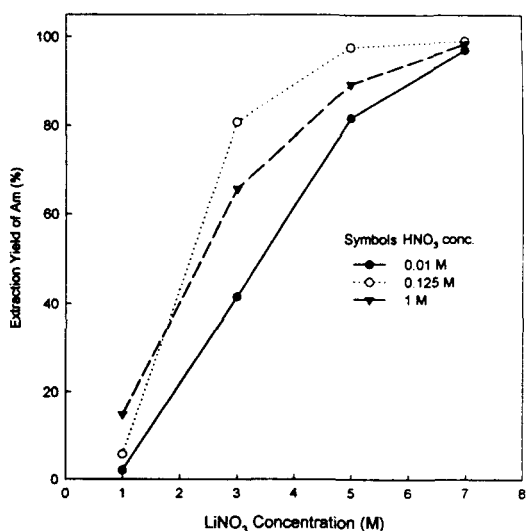


Fig. 5. Variation of the Extraction Yield of Am with LiNO₃ Concentration for Various HNO₃ Concentrations at [Picolinamide (C₈H₁₇)] = 2M.

extreme cases, such as very high concentration or low concentration of LiNO₃, the extraction yield of Nd, Eu-152, and Am-241 is too high or low, respectively, indicating an improper separation efficiency. In this point of view, to improve this low efficiency, the use of 3.0M LiNO₃ is chosen to give a good selectivity for Am-241. The nitric acid concentration was determined to be 0.125M with which the optimized efficient separation was obtained.

5.3. Effect of Diluents and Additives

The influence of diluent species on metal ion extraction yield with LiNO₃ concentration is profiled in Figure 6. For Nd, Eu-152, and Am-241, benzene as a diluent gave the better extraction yield than did carbon tetrachloride. Figure 7 with regard to separation factors indicates that no matter what diluent species are used, Am-241 can be selectively separated over Eu-152 and Nd. In the case of using benzene as a diluent, the

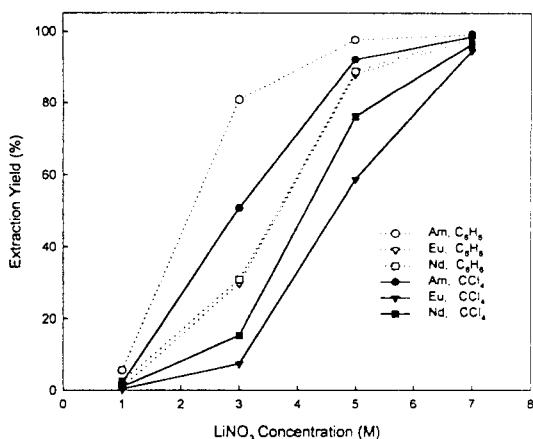


Fig. 6. Extraction Yields of Am, Eu and Nd with Changes of LiNO_3 Concentration for Different Diluents at [Picolinamide (C_8H_{17})] = 2M and $[\text{HNO}_3]=0.125\text{M}$

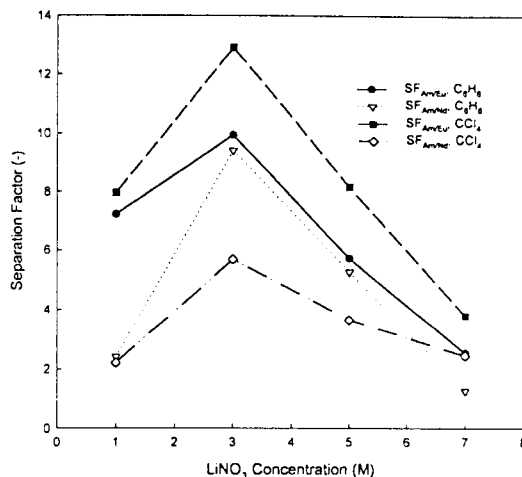


Fig. 7. Effect of LiNO_3 Concentration on the Separation Factors ($\text{SF}_{\text{Am}/\text{Eu}}$ and $\text{SF}_{\text{Am}/\text{Nd}}$) for Different Diluents at $[\text{HNO}_3] = 0.125\text{M}$ and [Picolinamide (C_8H_{17})] = 2M

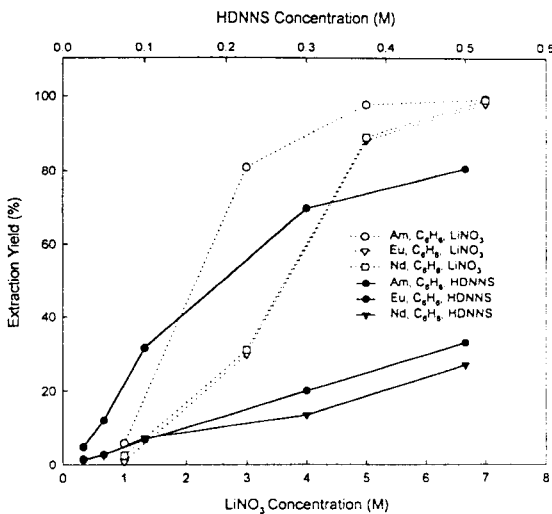


Fig. 8. Effect of LiNO_3 Concentration and HDNNS Concentration on the Extraction Yields of Am, Eu and Nd at [Picolinamide (C_8H_{17})] = 2M and $[\text{HNO}_3]=0.125\text{M}$

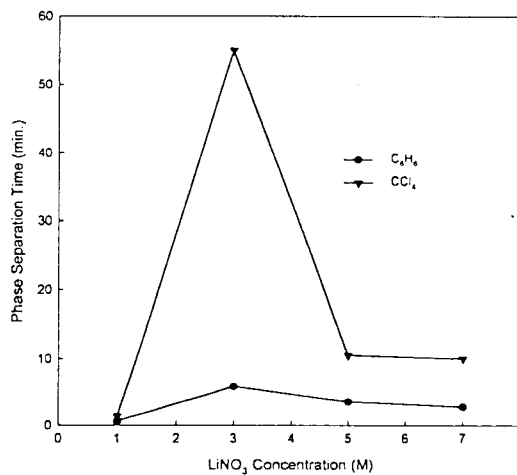


Fig. 9. Effect of LiNO_3 Concentration on the Phase Separation Time for Different Diluents at [Picolinamide (C_8H_{17})] = 2M and $[\text{HNO}_3] = 0.125\text{M}$

separation factors of Am-241/Eu-152 and Am-241/Nd are found to be 9.9 and 9.4, respectively. However, for carbon tetrachloride as a diluent, they are recorded as 12.9 and 5.70, respectively. So, benzene is more useful for this selective separation. It is because benzene

belongs to aromatic compounds but carbon tetrachloride belongs to aliphatic group, indicating that the former is more applicable for equation (2). Figure 8 describes the extraction yield profiles for Nd, Eu-152, and Am-241 influenced by LiNO_3 and HDNNS ($\text{HO}_3\text{SC}_{10}\text{H}_5$

(C₉H₁₉)₂) as additives. In the case of using benzene as a diluent, the use of LiNO₃ yields better results than that of HDNNS. This is probably due to two general facts : firstly, LiNO₃ as inorganic salt is soluble in an aqueous phase but HDNNS is soluble in an organic phase. Accordingly, secondly, decreased the fluidity and solubility of the organic phase, HDNNS can not be added beyond 0.50M.

5.4. Effect of LiNO₃ Concentration on Phase Separation Time

Figure 9 was profiled for phase separation time through variations of LiNO₃ concentration with 2.0M picolinamide(C₈H₁₇) and 0.125M nitric acid.

As the LiNO₃ concentration was increased, the separation time was observed to gradually increase till 3.0M LiNO₃, then it decreased. As a result, in the case of using 3.0M LiNO₃ with which the best separation of Nd, Eu-152, and Am-241 was observed, the separation time for benzene and carbon tetrachloride as a diluent was 5 min 50 secs and 55 mins, respectively. This result could be explained by the fact that a sufficient amount of nitrate salt (over 3.0M LiNO₃) can also react as indicated in the equation (3) to give fast separation. It is also due to the better solubility of an extracted metal salt in benzene than in carbon tetrachloride.

6. Conclusions

The experimental results for the extraction of Nd, Eu-152, and Am-241 using picolinamide (C₈H₁₇) as an extractant are as follows. Use of 0.125M nitric acid medium, 3.0M LiNO₃, 2.0M picolinamide(C₈H₁₇) yielded a good separation efficiency. Benzene as a diluent gave better phase separation than did carbon tetrachloride. In the case of using benzene as a diluent, the use of LiNO₃ provided a better result than did HDNNS.

With the above experimental conditions, the extraction yield of Nd, Eu-152, and Am-241 were calculated to be 30.9%, 29.8%, and 80.8%, respectively. In addition, a separation factor of Am-241/Eu-152 and Am-241/Nd were found to be 9.9 and 9.4, respectively. From these points of view, we could conclude that the synthesized organic chelating agent picolinamide(C₈H₁₇) has great potential in selective separation of actinide elements over lanthanide elements.

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