

Extraction of Lanthanide/Actinide with N,N'-Dimethyl-N,N'-dibutyltetradecylmalonic diamide (DMDBTDMA)

Han Beom Yang¹, Eil Hee Lee¹ and Jong Seung Kim²

¹Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon, 305-353, Korea

²Dankook University, San 8, Hannam-dong, Youongsan-gu, Seoul, 140-714, Korea
nhbyang@kaeri.re.kr

1. Introduction

It is known that a diamide extractant has a good extractability for the trivalent actinides and lanthanides elements. The amide is also advantageous for the treatment of radioactive waste, because diamide contains only C, H, O, N atoms and no phosphorus atoms, so that the spent solvent is completely incinerable and produces limited amounts of secondary waste combustion. Furthermore, the radiolytic stabilities of malonic acid diamides are sufficient enough for use in radioactive waste treatment and diamide is easy to synthesize. The malonamide, DMDBTDMA (N,N'-dimethyl dibutyl tetradecyl malonamide, (C₄H₉(CH₃)NCO)₂ CHC₁₄H₂₉) has shown very promising extraction properties [1-6]. In this paper, the extraction behaviours of the actinides (Am, Np) and lanthanides (Eu, Nd, La) elements by DMDBTDMA dissolved in dodecane were investigated.

2. Experimental

2.1 Reagents

DMDBTDMA is not commercially available, so it was synthesized by J. S. Kim [7]. DMDBTDMA was synthesized in two steps: in the first step, a synthetic precursor, N,N'-dimethyl-N,N'-dibutylmalondiamide was synthesized for a 65% yield by the use of an autoclave. In the second step, the final product, N, N'-dimethyl-N, N'-dibutyl tetradecyl malondiamide was synthesized for a 65% yield from the reaction of N, N'-dimethyl-N, N'-dibutyl malondiamide and 1-bromotetradecane. The final product compound was proved by a ¹H-NMR spectrum, ¹³C-NMR spectrum and an Infra-red spectrum. Other commonly used chemicals are Merck analytical grade reagents, without any further purification. Radioisotope tracers (²⁴¹Am, ¹⁵²Eu, ²³⁷Np) were obtained from the AEA technology company of England.

2.2 Equilibrium Measurements

1 mL of an aqueous phase containing a tracer amount of the radioisotopes (²⁴¹Am, ¹⁵²Eu, ²³⁷Np) or a 20 – 100 ppm concentration of the non-radioisotope elements (Nd, La, Ce, Y) in nitric acid of varying concentrations and 1 mL of an organic phase containing various concentrations of DMDBTDMA in dodecane were shaken in a shaker (Jeio Tech. Co., model : SI-900R) for 1 hour. After a phase separation by gravity, the samples

taken from the both phases were analyzed by gamma spectrometry (multichannel analyzer, Oxford Co. with Ge(Li) detector) for the radioisotopes and by ICP (Jovin-yvon, model JY 38 plus) for the non-radioisotopes elements. An aqueous nitric acid concentration at an equilibrium was measured by titration with a sodium hydroxide solution. The organic nitric acid concentration at an equilibrium was measured by titration with a sodium hydroxide solution after stripping the organic phase with pure water.

3. Results and discussion

3.1 HNO₃ extraction

The results of the HNO₃ extraction between DMDBTDMA in dodecane and an aqueous nitric acid have a similar behaviour pattern to that of the result measured in the TPH diluent [1, 4]. The concentration ratio C_{HNO₃}/C_{DMDBTDMA} varies between 0.2 and 2.

3.2 Third phase formation

The effects of several parameters, the concentration of DMDBTDMA in dodecane, temperature, metal ion concentration, HNO₃ concentration and aromatic diluent (decane) on the third phase formation was studied. In the case of the metal ion concentration and HNO₃ concentration they were increased, and the third phase formation was observed, but for the temperature, as the temperature was increasing the third phase formation phenomena was decreasing. For the aromatic diluent (decane), the third phase formation was not observed.

3.3 Extraction of Actinide/Lanthanide

Figure 1 shows the extraction yields (%) of various metallic nitrates of interest as a function of the nitric acidity at an equilibrium during extraction by 0.5M DMDBTDMA in dodecane. For all the elements, an increase in the aqueous nitric acid concentration caused an increase in the extraction yields. Figure 1 also shows that Am(III) and Eu(III) nitrates are extracted better than the Np(V) nitrate. The affinity sequence is as follows: Am(III) > Eu(III), Nd(III), La(III) > Np(V). The back-extraction from the loaded organic phase was performed with a 0.5M nitric acid solution and the Am(III) recovery yield was more than 99% in one batch experiment.

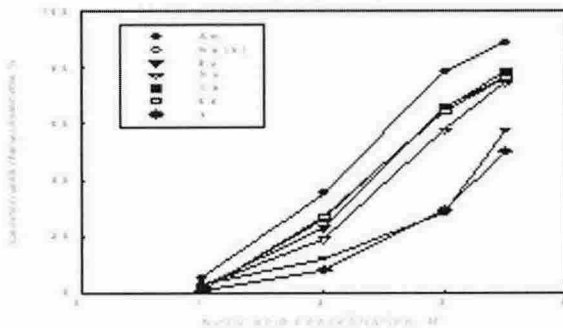


Figure 1. Extraction of Am, Np, Eu, Ce, La and Y by 0.5M DMBTDMA/dodecane from a nitric acid solution.

3.4 Effect of the diluents on the metal extraction

As shown in Figure 2, aliphatic solvent dodecane provided higher extraction yields than aromatic solvent decaline. Dodecane has some problems in the third phase formation when compared with the decaline, but in the extraction efficiency it is better than the decaline.

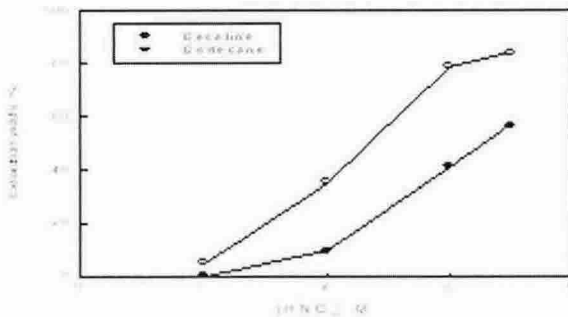


Figure 2. Effect of the diluent on the Am(III) extraction by 0.5M DMBTDMA from a 3.5M nitric acid solution.

3.5 Thermal stability of DMBTDMA

For the thermal stability test of the extractant, 1mL of 0.5M DMBTDMA in the dodecane solution and 1 mL of

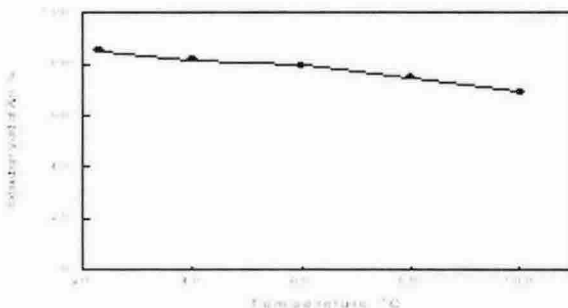


Figure 3. Extraction of Am by the thermally treated 0.5M DMBTDMA/dodecane from a 3.5M nitric acid solution.

a 3.5M nitric acid solution was taken in a glass vial and exposed to a thermal treatment in the oven (Scien Co., with temperature controller) at the experimental conditions and temperature for an hour. The extractant was used for the extraction of ²⁴¹Am after cooling. As the thermal treatment temperature was increasing, the extraction yields of Am were decreasing more rapidly as shown in Figure 2.

3. Conclusion

The extracting properties of DMBTDMA regarding the actinide and lanthanide elements are briefly described in this paper. The main results of the actinide and lanthanide extraction and back-extraction provided generally good solvent extraction properties. However, a number of problems, such as the third phase formation phenomena and low metal ion loading capacities without a third phase formation, were identified. For the development of the problems of DMBTDMA extractant, some of the new diamide extractants displaying improved extracting properties have to be synthesized and study.

REFERENCES

- [1] L. Nigond, Proprietes extractantes des N, N, N', N'-tetraalkyl-alkyl-2 propanediamides-1,3, CEA-R-5610, 1992.
- [2] L. Nigond, C. Musikas, and C. Cuillerdier, "Extraction by N,N,N',N'-tetraalkyl-2 alkylpropane-1,3-diamides, II. U(VI) and Pu(IV)", Solvent Extraction and Ion Exchange, Vol. 12(2), 297-323 (1994).
- [3] L. Nigond, N. Condamines, P.Y. Cordier, J. Livet, C. Madic, C. Cuillerdier, C. Musikas, "Recent advances in the treatment of nuclear wastes by the use of diamide and picolinamide Extractants", Sep. Sci. and Tech., Vol. 30(7-9), 2075-2099 (1995).
- [4] L. Nigond, C. Musikas, and C. Cuillerdier, "Extraction N, N, N',N'- tetraalkyl - 2 alkylpropane - 1, 3 - diamides, I. H₂O, HNO₃ and HClO₄", Solvent Extraction and Ion Exchange, Vol. 12(2), 261-296 (1994).
- [5] O. Courson, M. Lebrun, R. Malmbeck, G. Pagliosa, K. Romer, B. Satmark and J. P. Glatz, "Partitioning of Minor Actinides from HLLW Using the DIAMEX Process. Part 1", Radiochim Acta, Vol. 88, 857-863 (2000).
- [6] R. Malmbeck, O. Courson, G. Pagliosa, K. Romer, B. Satmark, J. P. Glatz, and P. Baron., "Partitioning of Minor Actinides from HLLW Using the DIAMEX Process. Part 2", Radiochim Acta, Vol. 88, 865-871 (2000).
- [7] J. S. Kim, "Synthesis of diamides for actinide and lanthanide metals", KAERI/CM-382/99, 1999.