Studies on a hydrolysis and radiolysis of DMDBTDMA

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1. Introduction

DMDBTDMA (N, N'-dimethyl, N, N'-dibutyl tetra decyl malonamide) is used as extractant in the DIAMEX (DIAMide Extraction) process. DMDBTDMA is used for the removal of long-lived radionuclide of minor actinide elements from nuclear wastes in order to transmute them into short-lived nuclide. DMDBTDMA is a completely incinerable CHON compound and does not generate large amounts of waste. DMDBTDMA is synthesized in our laboratory and several tests were performed to check the extractants resistance to hydrolysis by nitric acid, a thermal decomposition by heat and a radiolysis by gamma ray. DMDBTDMA could be applied to the extraction of actinide elements with a more effective separation ability, selectivity and a reduction of a second waste. Radiation damage to amide compound used as a extractant for actinide nuclides can markedly influence a process efficiency. Damage to solvents may result in emulsifiers or species which form insoluble or no extractable complexes with metal ions. When the mixture solvent of a extractant and diluent is used in high level radiation environments, the relationship of the dose level to the radiation damage must be known, as well as the relationship of this damage to the process efficiency. In the present studies, DMDBTDMA was synthesized in our laboratory and several tests were performed to check the extractant resistance to a hydrolysis by nitric acid, a thermal decomposition by heat and a radiolysis by gamma ray.

2. Methods and Results

2.1 Synthesis of DMDBTDMA

In the first step, synthetic precursor, N, N'-dimethyl-N, N'-dibutylmalondiamide was synthesized by the use of a autoclave apparatus. In the second step, final product of DMDBTDMA was synthesized by the introduction of the $C_{14}H_{29}$ group to α – carbon of the carbonyl group in the precursor compound. The final product of DMDBTDMA was confirmed by ^{1}H NMR, ^{13}C NMR (nuclear magnetic resonance) spectroscopy and infrad-red spectroscopy.

2.2 Hydrolysis of DMDBTDMA by HNO_3

Concerning the hydrolysis, even after the solution of 0.5M DMDBTDMA in dodecane had been occasionally stirred with a equal volume of aqueous 3.5M HNO_3 in a glass Erlenmeyer flask at room temperature for 38 days, either a discernible decrease in the extractability of DMDBTDMA or the formation of any degradation products was not observed. It was concluded that DMDBTDMA was hydrolytically stable at room temperature in this experimental condition.
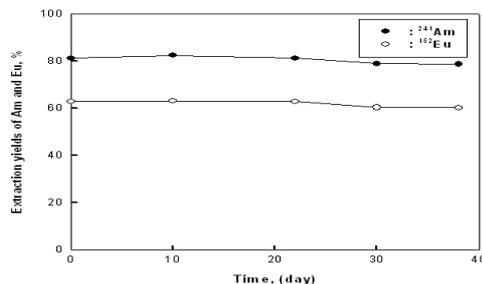

Figure 1. Hydrolytic stability of DMDBTDMA in 0.5M DMDTDMA -dodecane-3.5M HNO_3 system.

2.3 Thermal stability of DMDBTDMA

DMDBTDMA was thermally treated at 25, 40, 60, 80 and 100°C and the concentration of DMDBTDMA was determined by GC. GC system was Hp 5890 series II gas chromatography with analytical column (DB-1HT (15m x 0.32 mm x 0.1 μm) capillary and a FID detector. The extractability change of DMDBTDMA was checked by a solvent extraction of ^{241}Am and ^{152}Eu nuclide with the thermally treated DMDBTDMA in a 0.5M DMDTDMA/ dodecane - 3.5 M HNO_3 system. ^{241}Am and ^{152}Eu were analyzed by a MCA with Ge(Li) detector. The thermal decomposition of DMDBTDMA was start a over the 80°C as shown in Figure 2. The behavior of thermal decomposition and the extractability change of the DMDBTDMA are similar pattern as shown in Figure 2.
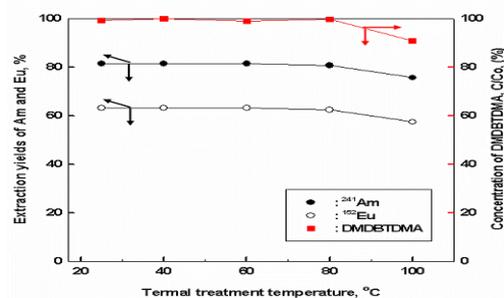

Figure 2. Thermal stability of DMDBTDMA and extractability change of ^{241}Am and ^{152}Eu in 0.5M DMDTDMA/dodecane-3.5 M HNO_3 system.

2.4 Radiolytic stability of DMDBTDMA

DMDBTDMA samples were prepared in a 20 mL glass scintillation vial with a screw type cap (Polyseal liner cone type) for a irradiation. The DMDBTDMA samples were irradiated with gamma ray from ^{60}Co source (95,000 Ci) in air at a room temperature condition in a irradiation facility of KAERI. The concentration of DMDBTDMA was determined by a gas chromatography (Hp 5890 series II). The GC/MS spectrum of the gamma ray irradiated DMDBTDMA ($1x10^6$ Gy) is shown in Figure 3. The results of the concentration of DMDBTDMA determined by GC in the gamma ray irradiated DMDBTDMA samples are summarized in Table 1. These results indicate that the bonds of DMDBTDMA are likely to be broken by a gamma irradiation and produce many degradated and fragmented compounds as shown in Figure 3. Table 1 shows a wide range of radiolytic degradations, from a low fractional decomposition to a high fractional decomposition. The radiolysis degradation of DMDBTDMA was notably increased by more than $1x10^6$ Gy of the absorbed dose.
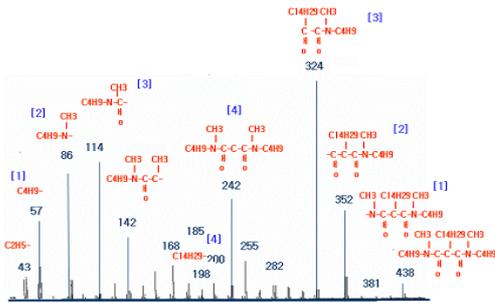

Figure 3. GC/MS spectrum of gamma ray irradiated DMDBTDMA ($1x10^6$ Gy)

Table 1 Concentration of DMDBTDMA determined by GC in gamma ray irradiated DMDBTDMA samples.

Irradiation, Gy	DMDBTDMA	
	Concentration, %	Fractional decomposition
0	100.0 %	0.0000
$1x10^3$	99.98 %	0.0002
$1x10^4$	99.95 %	0.0005
$1x10^5$	99.93 %	0.0007
$1x10^6$	95.92 %	0.0408
$2x10^6$	90.38 %	0.0962

2.5 Calculation of radiation reaction yield (G value) of DMDBTDMA

The fractional decomposition of TBP [1] is calculated as equation (1).

f (-TBP) = [2.247 x 1022 eV/Wh]/(6.023 x 10^{23} molecules / mole)] x GDM /ρ = 3.73 x 10^{-4} GDM/ρ (1)

where G = radiation reaction yield (molecules/100 eV), D = dose (Wh/L), M = molecular weight (g/mol), and density (g/L).

The concentration and fractional decomposition of DMDBTDMA as a function of the irradiation dose are recorded in Table 1. The fractional decomposition of DMDBTDMA after a irradiation at a low dose ($1x10^3$ Gy) and at a high dose ($2x10^6$Gy) are 0.0002 and 0.0962, respectively. [Table 1]

(a) f (-DMDBTDMA) = 0.0002, at $1x10^3$ Gy
 0.0002 = $3.73x10^{-4}$ x G x 0.28 x 483.73 x (1/1016)
 = 4.97 x 10^{-5} x G, $\therefore$ G = 4.02 $\fallingdotseq$ 4
(b) f (-DMDBTDMA) = 0.0962, at $2x10^6$ Gy
 0.0962 = $3.73x10^{-4}$ x G x 555.5 x 483.73 x (1/1016)
 = 9.86 x 10^{-2} x G, $\therefore$ G = 0.975 $\fallingdotseq$ 1

The G values of the other irradiated doses are 10, 1.4 and 0.83 at $1x10^4$ Gy, $1x10^5$ Gy and $1x10^6$ Gy, respectively.
Where, D=0.28Wh/L (at $1x10^3$ Gy) and 555.5Wh/L (at $2x10^6$ Gy), M = 483.73 g/mol, ρ =1016 g/L. The G value for the degradation of TBP [1] is 1–3 molecules/100eV and that of TODGA [2] is 8.5 ± 0.9 molecules/100eV.

3. Conclusion

DMDBTDMA is synthesized in our laboratory and several tests were performed to check the extractant resistance to a hydrolysis by nitric acid, a thermal decomposition by heat and a radiolysis by gamma ray. Hydrolysis by 3.5M nitric acid was not observed for 38 days and a thermal decomposition was started at the 80 ^{o}C whereas a radiolysis by gamma irradiation was notably observed at $2x10^6$ Gy. The G-value for a degradation of neat DMDBTDMA was 1-10. The hydrolytic, thermal and radiolysis stabilities of DMDBTDMA are sufficient for use in nuclear waste treatments.

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