Synthesis ofN,N' -dimethyl-N,N' -didecyl-3-oxa-diglycolamide for extraction of lanthanides postprint

Authors: ZHANG Liao-Ning, Ya-Qun Wang, SUN Guo-Xin, ZHOU He-Fang, DANG Qing-Yi, CUI Yu

Date: 2023-06-18T00:00:00+00:00

Abstract

A novel extractant, N,N' -dimethyl-N,N' -didecyl-3-oxa-diglycolamide (DMDDDGA), was designed and synthesized for extraction of lanthanides in the nuclear fuel reprocessing. The extraction behaviors of Gd, Dy, Er and Ho from nitric acid solution were investigated using DMDDDGA in chloroform. The effects of nitric acid concentration, extractant concentration, and temperature on the extraction were investigated. The distribution ratio of lanthanides increases with concentrations of the extractant and nitric acid, but decreases with increasing temperature, which indicates that the extraction process is exothermic. FT-IR spectra indicated that the C=O in DMDDDGA is coordinated with metal ion in the extracted species and the stoichiometries of lanthanides(III) complex are Gd(NO3)3 3DMDDDGA, Dy(NO3)3 4DMDDDGA, Er(NO3)3 4DMDDDGA, and Ho(NO3)3 4DMDDDGA.

Full Text

Preamble

NUCLEAR SCIENCE AND TECHNIQUES 25, 040301 (2014)

Synthesis of N,N -dimethyl-N,N -didecyl-3-oxa-diglycolamide for extraction of lanthanides

ZHANG Liao-Ning, WANG Ya-Qun, SUN Guo-Xin, ZHOU He-Fang, DANG Qing-Yi, and CUI Yu

School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

(Received December 13, 2013; accepted in revised form March 3, 2014; published online July 27, 2014)

Abstract: A novel extractant, N,N -dimethyl-N,N -didecyl-3-oxa-diglycolamide (DMDDDGA), was designed and synthesized for extraction of lanthanides in nuclear fuel reprocessing. The extraction behaviors of Gd, Dy, Er and Ho from nitric acid solution were investigated using DMDDDGA in chloroform. The effects of nitric acid concentration, extractant concentration, and temperature on the extraction were investigated. The distribution ratio of lanthanides increases with concentrations of the extractant and nitric acid, but decreases with increasing temperature, which indicates that the extraction process is exothermic. FT-IR spectra indicated that the C=O in DMDDDGA is coordinated with metal ion in the extracted species and the stoichiometries of lanthanides(III) complex are $Gd(NO_3)_3 \cdot 3DMDDDGA$, $Dy(NO_3)_3 \cdot 4DMDDDGA$, $Er(NO_3)_3 \cdot 4DMDDDGA$, and $Ho(NO_3)_3 \cdot 4DMDDDGA$.

Keywords: N,N -dimethyl-N,N -didecyl-3-oxa-diglycolamide, Extraction, Lanthanide, Nitric acid solution

DOI: 10.13538/j.1001-8042/nst.25.040301

Introduction

The separation of uranium, thorium and rare earth elements in reprocessing spent thorium-uranium fuel is an important issue. Lanthanide elements have large thermal neutron capture cross sections, which affect the thermal neutron transmutation of the long-lived fission products. Therefore, lanthanides must be separated from high-level waste in the Th-U fuel reprocessing cycle. The utilization of diglycolamides in the extraction of actinides, lanthanides, and other metals has attracted considerable interest. The 3-oxa-diglycolamide extractants with symmetrical substituent groups on the nitrogen atom, such as N,N,N ,N -tetraoctyl-3-oxa-diglycolamide (TODGA), have been studied extensively because of their complete incinerability and desirable coordination properties of oxygen to lanthanide and actinide ions. However, the large substituent alkyl group (octyl) connected to the nitrogen atom creates significant steric hindrance, which results in decreased extraction distribution ratios.

We have investigated the synthesis of unsymmetrical amides and their extraction properties for lanthanides, and found that N,N -dimethyl-N,N -dioctyl-3-oxa-diglycolamide (DMDODGA) showed higher affinity toward lanthanide ions than TODGA or N,N,N ,N -tetrabutyl-3-oxa-diglycolamide, as the symmetrical larger alkyl groups result in greater steric hindrance. In this paper, we report a new unsymmetrical extractant, N,N -dimethyl-N,N -didecyl-3-oxa-diglycolamide, with longer alkyl groups to improve the solubility of the diglycolamide and its adduct in the organic phase, and methyl groups to keep steric hindrance to a minimum. DMDDDGA is synthesized by a simple three-step route and the extraction behavior for lanthanides(III) is investigated. The results show that the designed extractant has strong extraction capability for lanthanides(III).

Experimental

A. Reagents and Experimental Equipment

All chemicals were of reagent grade. Carbon, hydrogen, and nitrogen were analyzed by a Perkin-Elmer PE2400C elemental analyzer. IR spectra were recorded at 4000–500 cm^{-1} with KBr discs on a Bio-Rad FTS-165 spectrometer. The ^1H NMR was obtained with a Bruker DPX-400 NMR. DMDDDGA was synthesized in the following three steps [Figure 1: see original paper].

Fig. 1. Synthesis scheme of DMDDDGA.

1. N-methyl decyl amine

1-Bromodecane (25 mL, 0.12 mol) and 175 mL of 30% methylamine alcohol solution were stirred at 110 °C for 48 h in a 200-mL autoclave. The methylamine alcohol solution was removed by distillation and the residue was distilled (236–238 °C/0.1 MPa) to give 14.36 g N-methyl decyl amine, with a yield of 70%. IR (cm^{-1}/film): 3286, 2927, 2853, 2789, 1463 and 724. ^1H NMR (400 MHz, $CDCl_3$): δ 2.479-2.449 (m, 2H, CH_2NH), 2.351-2.290 (m, 3H, $NHCH_3$), 1.372 (s, 2H, CH_2CH_2NH), 1.182 (s, 14H, $(CH_2)_7$), 1.087 (s, 1H, NH), 0.802-0.772 (m, 3H, CH_2CH_3).

2. Diglycoloyl chloride

A mixture of diglycolic acid (34.4 g, 0.26 mol), thionyl chloride (220 mL, 370 g, 3.08 mol), and a few drops of pyridine were stirred at reflux for 5 h. The thionyl chloride was removed by distillation and the residue was distilled to produce diglycoloyl chloride (39 g) as yellow oil (85-88 °C/5 kPa), with a yield of 87% [17].

3. Synthesis of DMDDDGA

N-methyl decyl amine (120 g, 0.7 mol), pyridine (56.5 mL, 0.7 mol) and benzene (200 mL) were mixed and cooled to 5 °C. Then, 34 mL of diglycoloyl chloride (0.28 mol) dissolved in benzene (50 mL) was added dropwise under stirring. The reaction was kept for 2 h in an ice bath and 1 h at ambient temperature. The residue was filtered and the filtrate was washed with 1 mol/dm^3 HCl, 3 mol/dm^3 NaOH, and water, successively. The organic phase was dried over anhydrous Na_2SO_4. Benzene was removed by distillation and DMDDDGA, a reddish brown oil (183.5 g), was obtained by column chromatography, with a yield of 56%.

IR (cm^{-1}/film): 2926, 2855, 1660, 1467, 1399 and 1122. ^1H NMR (400 MHz, $CDCl_3$): δ 4.273 (d, 4H, CH_2OCH_2), 3.335-3.183 (m, 4H, NCH_2), 2.909 (d, 6H, NCH_3), 1.498(s, 4H, NCH_2CH_2), 1.229(s, 28H, $(CH_2)_7$), and 0.862-0.833 (m, 6H, CH_2CH_3). Elemental analysis $C_{26}H_{52}N_2O_3$ (calculated values are shown in brackets): C 70.87% (70.86%), H 11.20% (11.89%), and N 6.23% (6.36%).

B. Extraction Procedure

Equal volumes of aqueous phase and organic phase were agitated for 30 min to obtain equilibrium at a constant temperature. The two phases were centrifuged and assayed by taking known aliquots (0.05-0.10 mL) from the aqueous phase. The M^{3+} content in the aqueous phase was determined by Arsenazo-III visible spectrophotometric analysis, and the M^{3+} content in the organic phase was obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of M^{3+}. The distribution ratio (D) was calculated as the ratio of the concentration of M^{3+} in the organic phase to that in the aqueous phase.

C. FT-IR Characterization

Equal volumes of 0.20 mol/dm^3 DMDDDGA solution and 0.05 mol/dm^3 of trivalent lanthanide ions were agitated. FT-IR spectra of the organic phase were recorded using a potassium bromide window with scanning times of 16 and a resolution of 2 cm^{-1}.

Results and Discussion

A. Effect of HNO_3 Content on Distribution Ratio

The extraction of lanthanides(III) from nitric acid medium was studied using DMDDDGA within the initial nitric acid concentration range of 1.0-3.5 mol/dm^3 [Figure 2: see original paper].

Fig. 2. Effect of HNO_3 concentration on extraction of lanthanides. C_M^{3+} = 5.00×10^{-3} mol/dm^3, C_{DMDDDGA} = 0.05 mol/dm^3, 298 K.

Nitric acid concentration has little effect on the distribution ratio in the range of 1.0-2.0 mol/dm^3. The D value increases markedly with nitric acid concentration above 2.0 mol/dm^3, indicating that the anion NO_3^- plays an important co-ion role in this extraction system. Figure 2 also shows that the extraction behavior of DMDDDGA for Gd(III), Dy(III), Ho(III) and Er(III) follows a positive sequence with atomic number. Shimojo et al. [19] also found similar phenomena where heavier lanthanide cations were more effectively extracted.

B. Effect of DMDDDGA Content on Extraction

The extraction of trivalent lanthanide elements (M^{3+}) from HNO_3 solution by DMDDDGA can be expressed as:

$$M^{3+} + 3NO_3^- + n\text{DMDDDGA} = M(NO_3)_3 \cdot n\text{DMDDDGA}$$

The extraction equilibrium constant is:

$$K_{ex} = \frac{a_{M(NO_3)_3 \cdot n\text{DMDDDGA}(o)}}{a_{M^{3+}} a^3_{NO_3^-} a^n_{\text{DMDDDGA}(o)}}$$

The conditional equilibrium constant is:

$$K = \frac{[M(NO_3)_3 \cdot n\text{DMDDDGA}]_{(o)}}{[M^{3+}][NO_3^-]^3[\text{DMDDDGA}]^n_{(o)}} \cdot \frac{\gamma_{M(NO_3)_3 \cdot n\text{DMDDDGA}(o)}}{\gamma_{M^{3+}}\gamma^3_{NO_3^-}}$$

where [M^{3+}] is the aqueous concentration of M^{3+}, and [M(NO$_3$)$_3$ · nDMDDDGA] is the concentration of extracted species in the organic phase. With a constant [NO$_3$$^-$], the equation can be rearranged by taking the logarithm:

$$\log D = \log K + n\log[\text{DMDDDGA}]_{(o)} - 3\log[NO_3^-]$$

From this equation, n can be estimated from the slope analysis of the relationship between log D and log[DMDDDGA] .

The effect of DMDDDGA concentration on the distribution ratio of lanthanides is shown in Figure 3. It can be seen that log D increases with DMDDDGA concentration, and the slopes are n = 4.02, 3.74, 3.64 and 3.03 for Er^{3+}, Ho^{3+}, Dy^{3+} and Gd^{3+}, respectively. Therefore, the stoichiometries of the main extracted species can be described as Gd(NO$_3$)$_3$ · 3DMDDDGA and M(NO$_3$)$_3$ · 4DMDDDGA (M = Dy^{3+}, Ho^{3+}, Er^{3+}). Similar variations in stoichiometry of the metal-ligand complex were corroborated by EXAFS studies [20] of Er^{3+}-DGA complex in ethanol, which suggested that only two of the four DGA molecules might be bonded in a tridentate fashion with some water molecules in the inner coordination sphere.

The extraction mechanism can be expressed as:

$$M^{3+} + 3NO_3^- + 3\text{DMDDDGA}_{(o)} = M(NO_3)_3 \cdot 3\text{DMDDDGA}_{(o)} \quad (M = Gd)$$

$$M^{3+} + 3NO_3^- + 4\text{DMDDDGA}_{(o)} = M(NO_3)_3 \cdot 4\text{DMDDDGA}_{(o)} \quad (M = Dy, Er, Ho)$$

The log K values for extracting Gd^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+} with DMDDDGA in chloroform from nitric acid, calculated using the equilibrium constant equation, were 3.10 ± 0.06, 4.84 ± 0.06, 5.03 ± 0.06 and 5.21 ± 0.07, respectively. The asymmetric DMDDDGA demonstrates better extraction efficiency than TBDGA in our previous work [21].

FT-IR spectra of the organic phase loaded with extracted species were recorded [Figure 4: see original paper]. The stretching frequency of the C=O band is shifted from 1660 to 1622 cm^{-1}. Sasaki et al. [22] also reported that the wave number of C=O shifts to lower values after extraction. The FT-IR results indicate that the carbonyl groups of DMDDDGA molecules are coordinated to metal ions. The wave number of C-O-C is shifted from 1122 cm^{-1} to 1126 cm^{-1}. Structural characterization of lanthanum(III) complex coordinated by diglycolamide (DGA) ligands shows that the ligand is tridentate [23].

Fig. 3. Effect of DMDDDGA concentration on extraction of lanthanides. C_{HNO}$_3$ = 2.5 mol/dm^3, C_M^{3+} = 5 × 10^{-3} mol/dm^3, 298 K.

Fig. 4. FT-IR spectra of organic phase loaded Ln(III) with DMDDDGA in chloroform.

C. Temperature Effect on Extraction

Figure 5 shows the temperature effect on the extraction distribution ratio. The extraction efficiency decreases with increasing temperature. From the Van' t Hoff equation [24], the thermodynamic parameters can be calculated:

$$\log D = -\frac{\Delta H}{2.303RT} + C$$

where R is the gas constant and C is a conditional constant. Therefore, -ΔH/(2.303R) represents the slopes in Figure 5. From this equation and Figure 5, we obtain ΔH = -36.57 kJ/mol, -38.87 kJ/mol, -42.70 kJ/mol and -46.34 kJ/mol for Gd^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+}, respectively, which indicates that the extraction reactions are exothermic.

Fig. 5. log D vs. 1/T for extraction of lanthanides(III) with DMDDDGA. C_M^{3+} = 5 × 10^{-3} mol/dm^3, C_{HNO}$_3$ = 2.5 mol/dm^3, C_{DMDDDGA} = 0.05 mol/dm^3.

Conclusion

The novel unsymmetrical extractant DMDDDGA has been successfully synthesized by a simple three-step route. DMDDDGA shows high affinity for lanthanides and good extraction capability from nitric acid solutions. The extraction distribution ratio increases sharply with HNO_3 concentration above 2 mol/dm^3 and with DMDDDGA concentration. The extracted complexes are $Gd(NO_3)_3 \cdot 3$DMDDDGA and $M(NO_3)_3 \cdot 4$DMDDDGA (M = Dy^{3+}, Ho^{3+} and Er^{3+}). Temperature has a significant effect on lanthanides(III) extraction. The extraction process is exothermic with reaction enthalpies of -36.57 kJ/mol, -38.87 kJ/mol, -42.70 kJ/mol and -46.34 kJ/mol for Gd^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+}, respectively. FT-IR spectra indicate that the carbonyl groups of DMDDDGA molecules are coordinated to metal ions. The extraction behavior of DMDDDGA for Gd(III), Dy(III), Ho(III) and Er(III) follows a positive sequence with atomic number.

References

[1] Mowafy E A and Aly H F. Solvent Extr Ion Exc, 2006, 24: 2002-2015.
[2] Mowafy E A and Aly H F. Solvent Extr Ion Exc, 2007, 25: 49-60.
[3] Modolo G, Asp H, Vijgen H, et al. Solvent Extr Ion Exc, 2008, 26: 62-76.
[4] Magnusson D, Christiansen B, Glatz J P, et al. Solvent Extr Ion Exc, 2009, 27: 26-35.
[5] Sasaki Y, Rapold P, Arisaka M, et al. Solvent Extr Ion Exc, 2007, 25: 187-204.
[6] Pathak P N, Ansari S A, Godbole S V, et al. Spectrochim Acta A, 2009, 73: 348-352.
[7] Zhu Z X, Sasaki S, Suzuki H, et al. Anal Chim Acta, 2004, 527: 163-168.
[8] Ansari S A, Pathak P N, Husain M, et al. Solvent Extr Ion Exc, 2005, 23: 463-479.
[9] Modolo G, Asp H, Schreinemachers C, et al. Solvent Extr Ion Exc, 2007, 25: 703-721.
[10] Ansari S A, Prabhu D R, Gujar R B, et al. Sep Purif Technol, 2009, 66: 118-124.
[11] Magnusson D, Geist A, Wilden A, et al. Solvent Extr Ion Exc, 2013, 31: 1-11.
[12] Bell J R, Luo H M, Dai S. Separ Sci Technol, 2012, 47: 2002-2011.
[13] Gujar R B, Ansari S A, Prabhu D R, et al. Solvent Extr Ion Exc, 2012, 30: 156-170.
[14] Pan Y F and Hussey C L. Inorg Chem, 2013, 52: 3241-3252.
[15] Panja S, Mohapatrab P K, Tripathi S C, et al. J Hazard Mater, 2012, 237-238: 339-346.
[16] Gujar R B, Ansari S A, Bhattacharyya A, et al. Solvent Extr Ion Exc, 2012, 30: 278-290.
[17] Sun G X, Liu M, Cui Y, et al. Solvent Extr Ion Exc, 2010, 28: 439-452.
[18] Cui Y, Yang J H, Yang G, et al. Hydrometallurgy, 2012, 121-124: 16-21.
[19] Shimojo K, Kurahashi K, Naganawa H. Dalton T, 2008, 37: 3811-3819.
[20] Ansari S A, Pathak P, Mohapatra P K, et al. Chem Rev, 2012, 112: 1751-1772.
[21] Teresa M M, Amparo G E, Jorge S Q, et al. Solvent Extr Ion Exc, 2009, 27: 107-131.
[22] Sasaki Y, Rapold P, Arisaka M, et al. Solvent Extr Ion Exc, 2007, 25: 187-204.
[23] Kannan S, Moody M A, Barnes C L, et al. Inorg Chem, 2008, 47: 4691-4695.
[24] Islam F, Rahman H, Ali M. J Inorg Nucl Chem, 1979, 41: 217-220.

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.