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AMIDES AS PHASE MODIFIERS FOR N,N'-TETRAALKYLMALONAMIDE EXTRACTION OF ACTINIDES AND LANTHANIDES FROM NITRIC ACID SOLUTIONS

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ABSTRACT

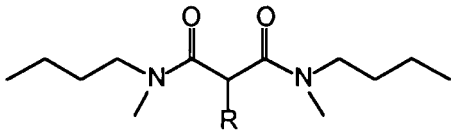
The N,N'-tetraalkylmalonamides are a class of compounds under development for transuranic (TRU) separations under high nitric acid conditions. There are several issues that challenge the further development of these ligands. One is the development of improved synthetic procedures that lend themselves to commercial scale-up. Another major issue is the third-phase formation that occurs when the N,N'-tetraalkylmalonamides are contacted with medium-to-high nitric acid concentrations in hydrocarbon solvents. To address the synthesis issue we have developed a new synthetic approach for preparing these materials. Third-phase formation can be eliminated by addition of diluent modifiers such as tributylphosphate (TBP). TBP is inappropriate if a nonphosphate-containing process stream is required. Amides have been proposed as alternatives for TBP in a variety of applications because of their ease of synthesis and the variety of substituents that can be generated. We have been able to develop an amide phase-modified system that extends the working process range of alkylmalonamides (0.5 M) in dodecane (unbranched hydrocarbon) from 3.5 M to 7.5 M nitric acid and in Isopar H (branched hydrocarbon) from 4.0 M to 10.0 M nitric acid using 1.0 M di-2-ethylhexylacetamide/0.5 M alkylmalonamide. The K_d values were comparable to extraction with alkylmalonamide in Isopar H or hydrogenated tetrapropylene (TPH) solvents. The overall extraction system was more robust than the phase-unmodified system allowing for greater temperature and acid concentration fluctuations without third-phase formation.

INTRODUCTION

The N,N'-tetraalkylmalonamides (1) are a class of compounds under development for transuranic (TRU) element separations in nitric acid solutions. There are several issues that challenge the further development of these ligands for use in reprocessing of spent nuclear fuel or treatment of nuclear wastes. Commercial production has been difficult as the reported synthesis does not lend itself to commercial scale-up. To address this issue we have developed a new synthetic approach to prepare the materials shown in Figure 1.

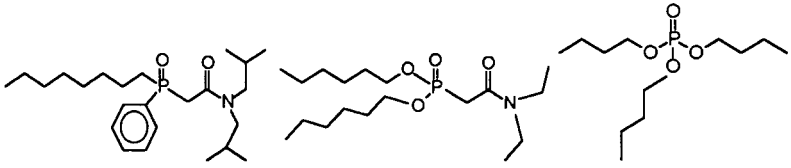
Another major challenge with using malonamides is the third-phase formation that occurs when the N,N'-tetraalkylmalonamides are contacted with medium-to-high nitric acid concentrations in high-boiling paraffinic-hydrocarbon solvents. Third-phase formation is the splitting of the organic phase into two parts, resulting in a light organic phase rich in diluent and lean in alkylmalonamide and a dense organic phase rich in alkylmalonamide-nitric acid complex. Third-phase formation is often eliminated by addition of diluent modifiers such as long-chain aliphatic alcohols that carry out specific solvation of the alkylmalonamide-nitric acid salt through either dipole-dipole interactions or hydrogen bonding. Hydrocarbon solvents are preferred for actinide processing because of their benign nature and extraction-enhancing capabilities (2, 3) when compared to aromatic and chlorinated solvents. Because the alkylmalonamides are weaker extractants for americium at lower acid concentrations (1-3 M) than other reported neutral, bidentate extractants (2- 6) such as CMP or CMPO (Figure 2), it is necessary to work at higher ligand and acid concentrations to obtain comparable extraction efficiencies. The amount of third-phase formation can be reduced by optimizing the substituents on the nitrogen and the alkyl group, R, on the alkylmalonamide. Musikas team (1) has found that by increasing the length of R from C-12 to C-14 and the alkyl amine substituents from C-4 to C-8, the amount of third-phase formation is reduced but not eliminated at higher nitric acid (5 M) concentrations.

Other neutral, bidentate extractants (CMP and CMPO) are reported to have third-phase formation problems in similar hydrocarbon solvents (3, 4). Phase modifiers were used to eliminate third-phase formation in these systems. The most common phase modifier is tri-n-butylphosphate (TBP) (Figure 2) (2-4). Although



(Compound I) when R = H
(Compound II) when R = $(CH_2)_{11}CH_3$
(Compound III) when R = $(CH_2)_{13}CH_3$
(Compound IV) when R = $(CH_2)_{19}CH_3$

FIGURE 1. Structures of selected alkylmalonamides



CMPO CMP TBP

(CMPO) octyl(phenyl)-N,N-diisobutylcarbamoylmethylenephosphine oxide
(CMP) dihexyl-N,N-diethylcarbamoylmethylenephosphonate
(TBP) tri-n-butylphosphate

FIGURE 2. Structure of CMPO, CMP, and TBP extractants.

this modifier might function to prevent third-phase formation with alkylmalonamides, the presence of a large concentration (≥1 M) of phosphorous-containing modifier defeats one of the major reasons for developing nonphosphorous-containing bidentate ligands in the first place; that is, to avoid a phosphorous-containing waste stream and to eliminate solvent regeneration steps to remove partially hydrolyzed phosphonates that can cause back-extraction problems in the processing of actinides (1, 7-11).

Amides have been proposed as alternatives for TBP in a variety of processes (10-14). We have proposed that amides could be used as phase modifiers for the alkylmalonamides similarly to how TBP is used for CMPO. The major problem

with amides is that some amides can also have third-phase formation problems at certain acid strengths (12-14). Because of the ease of amide synthesis and the variety of substituents that can be generated, it should be possible to develop a system that would be able to extend the working acid range of the alkylmalonamides. We report here the successful results of these studies.

EXPERIMENTAL

Apparatus. Instrumentation included nuclear magnetic resonance spectrometers (NMR, Varian Model EM 390, and Varian Model Gemini 200), a Fourier transform infrared (FTIR) spectrometer (Mattson Model Galaxy 5020), an ultraviolet (UV) diode array (Hewlett-Packard Model 8451A), a NaI well-type counter (MINAXI γ Auto-Gamma 5000), a gas chromatograph with flame ionization detector (GC-FID) (Hewlett-Packard Model 5710A, DB-1 column, 12 M, 0.2-mm bore, 0.33-μm coating; Hewlett-Packard Model 5890A, HP-5 column, 25 M, 0.2-mm bore, 0.32-μm coating), and a pH meter (Fisher Model 610A). Molecular weights were determined by GC-MS (Hewlett-Packard Model 5890 GC, Model 5970 MS, DB-5 column, 25 M, 0.2-mm bore, 0.32-μm coating).

Synthesis of Dibutyldimethylmalonamide (compound I). Freshly distilled diethylmalonate (40.5 g, 0.25 mol, Aldrich)[1] and N-methylbutylamine (110.2 g, 1.26 moles, Aldrich) were mixed together in an oven-dried glass container. The container was placed into a pressure vessel, which was sealed and placed in a 105°C oven for 3 days. The pressure vessel was then removed from the oven and allowed to cool to room temperature before being opened. Excess amine and ethanol were removed under vacuum to give 60 g of crude, pale-yellow product. The material was dissolved in $CHCl_3$ and washed twice with dilute HCl, once with dilute NaOH, and once with NaCl-saturated water. The organic phase was dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed under vacuum to give a heavy, oily material that solidified upon sitting. The material was recrystallized from

[1]Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, Milwaukee, Wisconsin 53233, USA

petroleum ether using freezer temperatures to encourage crystallization. It gave a white, crystalline material with a melting-point range of 48°C to 49°C. Considerable material was lost in the recrystallization, but second crops were obtained. An alternative purification was distillation at 140°C at 0.3 mm, but more than 50% of the material was lost to degradation.

The purity of the compound was verified by GC-FID to be > 98% (conditions: HP-5 column, starting T = 100°C, Final T = 290°C, Rate = 20°C/min, Total scan time = 25 min, compound retention time = 11.05 min.); ^{1}H NMR ($CHCl_3$-TMS): 0.884-0.985 ppm (6H, $C\underline{H}_3$-CH_2-, multiplet); 1.313-1.332 ppm (4H, CH_3-$C\underline{H}_2$-CH_2-CH_2-N, multiplet); 1.529-1.568 ppm (4H, CH_3-CH_2-$C\underline{H}_2$-CH_2-N, multiplet); 2.93 and 3.04-3.06 ppm (6H, $C\underline{H}_3$-N, singlet and doublet); 3.339-3.409 ppm (4H, $C\underline{H}_2$-N, multiplet); 3.48 ppm (2H, $[C(O)]_2$-$C\underline{H}_2$, singlet); FTIR(neat-melt): 2957, 2932, 2872, 1641 cm^{-1}

Synthesis of $C_{12}H_{25}$-substituted malonamide (compound II): Sodium hydride (3.3 g, 0.083 mol, 60% in mineral oil, Aldrich) was placed in an oven-dried, 3-neck, round-bottom flask fitted with a dry N_2 inlet and condenser. To remove the mineral oil, the flask was washed three times with small portions of hexane. Freshly distilled, tetrahydrofuran (THF, 100 mL over CaH) was added and the solution cooled to 0°C in an ice bath. A solution of the dibutyldimethylmalonamide (compound I, 20 g, 0.083 moles) in THF (50 mL) was added slowly over a half-hour and allowed to stir until it was mostly reacted. The reaction was completed when the temperature was allowed to rise to 10°C. 1-Bromododecane (20.5 g, 0.083 mol, Aldrich) was added all at once and the reaction mixture was allowed to stir at room temperature for 5 hour followed by refluxing for 1 hour. The THF was removed under vacuum, water was added to the reaction product, and the aqueous phase which was basic was extracted with hexane. The organic phase was then washed with dilute HCl and NaCl-saturated water, dried over anhydrous Na_2SO_4, filtered, and the hexane evaporated under vacuum to give 27 g of crude product. The material was placed on a silica gel column and eluted with hexane to remove any residual mineral oil and some by-products and starting material. The product was then eluted with

50:50 hexane:$CHCl_3$ to yield 20.4 g (60%) of 98% pure Compound II, according to gas chromatographic (GC) analysis. The product was soluble in dodecane ≥ 0.5 M.

The purity of the compound was verified by GC-FID to be > 98% (conditions: HP-5 Column, T = 290°C, Rt = 9.76 min.); FTIR(neat): 2925.2, 2854.8, 1649.2, 1465.9, 1402.3 cm^{-1}; MS peaks in descending relative abundance: 86 (base), 57, 114, 142, 296, 242, 324, 411 (M+1) m/e; ^1H NMR (TMS-$CHCl_3$): 0.83-1.02 ppm (9H, $C\underline{H}_3$-CH_2-, multiplet), 1.15-1.40 ppm (24H, CH_3-$C\underline{H}_2$-, multiplet), 1.42-1.58 ppm (4H, CH_3-CH_2-$C\underline{H}_2$-CH_2-N, multiplet), 1.82-1.95 ppm (2H, $C\underline{H}_2$-CH, multiplet), 2.95 and 2.98 ppm (6 H, $C\underline{H}_3$-N, doublet of doublets), 3.2-3.42 ppm (4H, CH_3-CH_2-CH_2-$C\underline{H}_2$-N-, multiplet), 3.48-3.60 ppm (1H, C-H, multiplet).

Synthesis of $C_{14}H_{29}$-substituted malonamide (compound III). The procedure described above was followed for this synthesis except that 1-bromotetradecane (22.9 g, 0.083 moles, Aldrich) was used. The crude product was 34.4 g (94% yield). After silica gel clean-up, a similar yield and purity was obtained. The product was soluble in dodecane ≥ 0.5 M.

The purity of the compound was verified by GC > 98% (conditions, HP-5 columns, T = 290°C, Rt = 15.9 min.); UV(ethanol): λ_{max} = 244nm; FTIR(neat): 2926.2, 2856.8, 1643.5, 1466.0, 1402.3 cm^{-1}; MS(peaks in descending relative abundance): 86 (base), 57, 114, 324, 242, 142, 352, 439 (M+1) m/e; ^1H NMR (TMS-$CHCl_3$): 0.835-0.972 ppm (9H, $C\underline{H}_3$-CH_2-, multiplet), 1.14-1.34 ppm (28H, CH_3-$C\underline{H}_2$-, multiplet), 1.458-1.536 ppm (4H, CH_3-CH_2-$C\underline{H}_2$- CH_2 -N, multiplet), 1.877-1.909 ppm (2H, CH-$C\underline{H}_2$-, multiplet), 2.95 and 2.98 ppm (6 H, $C\underline{H}_3$-N, doublet of doublets), 3.2-3.4 ppm (4H, CH_3-CH_2-CH_2-$C\underline{H}_2$-N-, multiplet), 3.48-3.60 ppm (1H, CH- CH_2multiplet).

Synthesis of $C_{20}H_{41}$-substituted malonamide (compound IV). The procedure described above was followed for this synthesis except that 1-bromoeicosane (29.9 g, 0.083 moles, Aldrich) was used. The crude product was 30.4 g (70% yield). After

silica gel clean-up, a similar yield and purity was obtained. This compound had lower dodecane solubility, ≈0.20 M.

Data on compound IV: UV(ethanol): λ_{max} = 242nm (has a shoulder about 280); FTIR(neat): 2919.1, 1642.3, 1465.8, 1403.1 cm^{-1}; ^{1}H-NMR (TMS-$CHCl_3$): 0.846-0.984 ppm (9H, $C\underline{H}_3$-CH_2-, multiplet), 1.16-1.36 ppm (40H, CH_3-$C\underline{H}_2$-, multiplet), 1.434-1.548 ppm (4H, CH_3-CH_2-$C\underline{H}_2$- CH_2-N, multiplet), 1.80-1.91 ppm (2H, CH-$C\underline{H}_2$-, multiplet), 2.973 and 2.986 ppm (6 H, $C\underline{H}_3$-N,doublet of doublet), 3.3-3.4 ppm (4H, CH_3-CH_2-CH_2-$C\underline{H}_2$-N-, multiplet), 3.48-3.60 ppm (1H, -CH-multiplet).

Synthesis of amides (compounds V, VI, VII) (10, 12, 13, 15). The N,N-dialkylamides were prepared according to the general procedure of Baldwin, et.al. (15), by adding a solution of the corresponding acyl chloride in dry diethyl ether to a cooled solution of the secondary amine in dry diethyl ether in the presence of triethylamine (TEA):

$RCOCl + HNR'R'' + (C_2H_5)_3N \rightarrow RCONR'R'' + (C_2H_5)_3NHCl$

The ether layer was washed with 20% NaCl, 2 M HCl, 2 M NaOH, and 20% NaCl to remove the TEA·HCl, any residual acyl chloride and any secondary amine. The solution was dried over anhydrous Na_2SO_4 overnight, the ether was removed under vacuum, and the amide was purified by vacuum distillation. Purity of the distillation fractions was determined by GC. The following disubstituted amides were prepared by the above procedure:

N,N-methyl-n-butylnonanamide (compound V): MS: 228 (M+), 114 (base); UV(ethanol): λ_{max} = 254 and 242 nm; FTIR(neat): 2957, 2927, 2857, 1649, 1465 cm^{-1}; ^{1}H NMR ($CDCl_3$-TMS): 3.26-3.36 ppm (2H, RC(O)N$C\underline{H}_2$, doublet of triplets), 2.98 and 2.91 ppm (3H, RC(O)N$C\underline{H}_3$, two singlets), 2.25-2.32 ppm (2H, -$C\underline{H}_2$C(O), doublet of triplet), 1.50-1.63 and 1.22-1.35 ppm (16H, R$C\underline{H}_2$-, multiplets), 0.84-0.99 ppm (6H, R$C\underline{H}_3$, multiplet).

N,N-dioctylacetamide (Compound VI): MS: 283 (M+), 142 (base); UV(ethanol): λ_{max} = 240 and 254 nm; FTIR(neat): 2925, 2860; 1642; 1461 cm^{-1}; ^{1}H NMR ($CDCl_3$-TMS): 3.16-3.32 ppm (4H, RC(O)N$C\underline{H}_2$, doublet of triplet), 2.060 ppm (3H,

$C\underline{H_3}C(O)$, singlet); 1.50-1.53 and 1.22-1.35 ppm (24H, $-C\underline{H_2}R$, multiplets), 0.84-0.92 ppm (6H, $RC\underline{H_3}$, multiplet).

N,N-di(2-ethylhexyl)acetamide (compound VII): MS: 283 (M+); 142 (base); UV(ethanol): λ_{max} = 240 nm; FTIR(neat): 2935, 2877; 1648; 1443 cm^{-1}; ^1H NMR ($CDCl_3$-TMS): 3.10-3.29 ppm (4H, $RC(O)NC\underline{H_2}$, multiplet, doublet), 2.08 ppm (3H, $-C\underline{H_3}C(O)$, singlet), 1.55-1.68 ppm (2H, R-C<u>H</u>-, multiplet), 1.18-1.38 ppm (16H, $C\underline{H_2}R$, multiplet), 0.81-0.94 ppm (12H, $RC\underline{H_3}$, multiplet).

GC with conditions. (Hewlett-Packard Model 5890A, HP-5 column, 25 M, 0.2-mm bore, 0.32-μm coating; Initial temperature = 100°C, Final temperature = 250°C, Rate = 8.0°C/min, Final time = 5 min): N,N-methyl-n-butylnonanamide: retention time = 18.30 min., N,N-dioctylacetamide: retention time = 23.92 min., N,N-di(2-ethylhexyl)acetamide: retention time = 20.28 min

Third-Phase Testing Procedure. The two alkylmalonamide extractants (C-14 and C-20; compound III and IV, respectively) and the amide phase modifiers were tested in a number of organic solvents by contacting with a range of nitric acid from 1 to 15.4 M. The organic solvents tested were cyclohexane, n-octane, 2,2,4-trimethylpentane, n-decane, n-dodecane, 1,4-diisopropylbenzene, Isopar H (a commercial isoparaffinic hydrocarbon blend from Exxon), and TPH (hydrogenated tetrapropylene, PROCHROM, Champignols, France). In general, the alkylmalonamide was at a concentration of 0.5 M, unless otherwise noted, except the C-20 malonamide (compound IV), which was tested at 0.2 M because of its lower solubility in dodecane. The amides were tested at a concentration of 1 M in the organic phase unless otherwise noted.

Testing was performed as follows: two milliliters of the organic phase containing either alkylmalonamide, amide, or a combination of both were contacted with two milliliters of the aqueous phase containing various nitric acid concentrations in four milliliter Wheaton glass vials with teflon seal caps. The solutions were shaken at room temperature (≈23°C) on a Burell Wrist-action Shaker for fifteen minutes at a setting of ten. The mixtures were allowed to settle, analyzed by visual inspection for a third phase, and then centrifuged in a Dynac II centrifuge

to aid phase separation at 1,500 rpm for ten minutes and examined again for the presence of the third phase.

Temperature Effect on Third Phase Formation. The effect of temperature on size and presence of the third (middle) phase (16) was tested as follows: a sample of 0.5 M C-14 alkylmalonamide (compound III) in Isopar H, which was exposed to 4.5 M nitric acid, was equilibrated in a water bath at 10°, 15°, 20°, 25°, 30°, 35°, and 40°C, mixed for 10 minutes on the wrist-action shaker and centrifuged for 5 minutes then visually examined for the presence and size of the third (middle) phase. The temperature was recorded between steps and the sample re-equilibrated in the water bath if necessary. The height of the third phase was measured and expressed as a percentage of the total height of the organic phase.

The effect of temperature and nitric acid concentration on size and presence of the third phase was tested as follows: samples of 0.5 M alkylmalonamide in TPH at 4, 4.5, 5, and 6 M nitric acid, 0.5 M C-14 malonamide and 0.5 M N,N-di(2-ethylhexyl)acetamide in dodecane at 4, 5, 5.5, and 6 M nitric acid, and 0.5 M C-14 malonamide and 1 M N,N-di(2-ethylhexyl)acetamide in TPH at 9, 9.5, 10, 11, and 12 M nitric acid were equilibrated in a water bath or refrigerator at 5.5°, 15°, 23° (room temperature), 30°, and 40°C (and 50°C for the alkylmalonamide in TPH alone), mixed for 10 minutes on the Wrist-action shaker and centrifuged for 5 minutes then visually examined for the presence and size of the third phase. The samples were re-equilibrated in the water bath between steps. The height of the third phase was measured and expressed as a percentage of the total height of the organic phase.

Distribution Studies of Amide and Malonamide Systems. Americium-241 was obtained from Los Alamos in-house supplies, europium-152 was obtained from the National Institute of Standards and natural abundance uranium from Aldrich. The radioisotope stock solution was prepared by fuming to dryness the isotope solution several times in HNO_3 and redissolving the tracer in dilute HNO_3. The solutions were spiked with the isotope concentrates such that the tracer concentrations were approximately 10^{-8} M. The 2 mL sample vials were shaken for 45 minutes and centrifuged for 2 minutes at 1,500 rpm. Two 0.5 mL aliquots were removed from

both phases and counted on a gamma counter for 10 minutes. Accountability for all extractions was 100±10%. The distribution ratio, K_d, was calculated as the net cpm/mL in the organic phase divided by the net cpm/mL in the aqueous phase.

RESULTS AND DISCUSSION

New synthetic Procedure for Alkylmalonamides. The ligands under study are depicted in Figure 1. Our ligand of choice (compound III) is based on the data collected by C. Musikas et. al. (1, 11) about the optimal substituent on both the carbonyl nitrogens and the methylene moiety. They found that an unsymmetrical pair of alkyl groups on the amide nitrogens, with one group being a methyl, gave the best extraction of americium. When the methylene substituent had an ether-linkage gamma to the methylene carbon, americium(III) extraction was optimized, but aqueous phase solubility and third-phase formation was increased (11, 14). There was also a trade off between optimizing actinide extraction and the difficulty and expense of ligand synthesis. According to the reported literature procedure, the ligand containing oxygens in the methylene tail were very difficult and time consuming to synthesize. We confirmed this in our attempts to replicate the synthetic procedure.

The synthetic procedures reported in the literature for these unsubstituted alkylmalonamides gave low yields. The procedures were difficult to perform because very air sensitive and caustic reagents were used (17). Our synthetic approach was based on work reported by J. G. H. DuPreez (private communication)[2], who reported that he could effect the amidation of a single ethyl ester in 5 hours at 60°C. The same conditions would effect only partial conversion of diethylmalonate to the malonamide. After considerable experimentation, we determined longer reaction times (3 days) and higher temperatures (105°C) were required to effect the desired transformation. Because the higher temperatures were above the boiling point of the N-methylbutylamine, we used a pressure reactor to

[2] J. G. H. DuPreez, Private Communication. Univ. of Port Elizabeth, Port Elizabeth, Republic of South Africa.

maintain the required temperatures. The pressure vessel permitted both the use of inexpensive and noncaustic reagents in this synthesis and ready scale-up of the starting material.

The second step of the synthesis as reported in the literature (17), used n-butyllithium as the base to deprotonate the malonamide, a relatively weak acid. n-Butyllithium is highly air sensitive and pyrophoric, making it difficult to perform large-scale reactions with this reagent. Attempts at using phase-transfer agents were reported (Charles Madic, private communication)[3], but purification of the final product was difficult. If any phase-transfer agent remained with the product, it interfered with the ligand's use as an extractant by acting as a surfactant.

Our approach was to use sodium hydride (NaH) as the base. The only by-product was a small amount of mineral oil that was readily removed or would not interfere with the extraction process in hydrocarbon diluents. Future syntheses could use mineral-oil-free reagent to by-pass this impurity. The NaH was relatively easy to handle, simplifying scale-up.

Our final purification for these substituted alkylmalonamides used pressure chromatography on silica gel. If one had a vacuum system that allowed for very high vacuums, the materials could be distilled. In general, though, we found that a considerable amount of material was lost due to degradation in our distillation process. For small-scale purification, chromatography was preferred.

We attempted an alternative synthetic approach to the substituted alkylmalonamides. In these attempts, diethylmalonate was treated with sodium hydroxide for deprotonation (diethylmalonate is a stronger acid than the malonamides and can be deprotonated with a weaker base) and then alkylated with an alkylbromide to form the methylene-substituted diethylmalonate. This crude product was readily purified by distillation because it has a lower boiling point than the substituted malonamide. The purified substituted diethylmalonate (an oil) was then placed in the pressure vessel and reacted with excess N-methylbutylamine in an attempt to form the alkylmalonamide. Higher temperatures (150°C) were required to effect uncatalyzed amide formation. At these higher temperatures,

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[3] Charles Madic, Private Communication. Commissariat a l'Energy Atomique, Fontenay-aux-Roses, Cedex, France.

decarboxylation occurred and about 50% of a monoamide (produced by hydrolysis and decarboxylation) was isolated along with the desired product. This approach has possibilities if the system could be catalyzed to cause the transformation to occur at lower temperatures. The approach has merit because NaOH is much cheaper and somewhat easier to handle than NaH.

All alkylmalonamides studied for this report were prepared by the new NaH procedure presented in the experimental section. They were prepared in greater than 98% purity according to GC. Molecular weight determinations were by GC-MS. MS fragmentation patterns and NMR, UV, and IR results were consistent with the structures of all compounds. To show the general nature of this synthetic procedure the alkyl groups on the malonamide was varied from C-12 to C-20. All the alkylmalonamides were colorless oils except C-20 which was waxy. It was also desirable to obtain the C-20 compound to determine if it had improved solubility properties in aliphatic solvents. It proved to have lower solubility in dodecane (0.2 M) than the C-14 compound (>0.5 M).

Reducing Third-Phase Formation. Amides have been proposed as alternatives for tri-n-butyl phosphate (TBP) in a variety of extraction processes (12). In general amides have similar or greater basicity than TBP, similar viscosities, solubilities, and hydrolytic and radiolytic stabilities. The amides generally have dipole moments similar to or greater than TBP (ε =7.959, μ = 3.07 at 30°C). The one major problem with amides is that they can have third-phase formation problems (12-14). An extensive literature search indicated that certain amides had greater dodecane solubility than others (12), and certain amide-uranium complexes gave minimum third-phase formation in such solvents as mesitylene. After reviewing the information, one commercially available amide, N,N-diethyldodecanamide (Aldrich, 98%), was obtained, and three candidate amides (N,N-methyl-n-butylnonanamide, N,N-dioctylacetamide, and N,N-di(2-ethylhexyl)acetamide) were synthesized for testing. The synthetic procedure for the amides used standard procedures and gave amides greater than 98% pure according to GC analysis. All spectral data was consistant with the amide structures.

The choice of which amides to test from the very large number of possibilities was based first on their commercial availability. We could find only

one amide which has low water solubility and high dodecane solubility and is commercially available. The other amides were chosen based on their basicity and dipole moments. It is known that the acetamides have a basicity close to that of TBP. If we want to reduce the chances of third-phase formation, we assumed that we would want to minimize the amount of nitric acid extracted into the organic phase. It was assumed that a ligand of lower basicity would have a better chance of doing this. Also, as dipole-dipole interactions might be responsible for disrupting third-phase formation, it would be desirable to have amides with high dipole moments. It does not appear from the literature that there is a clear structure-reactivity relationship for the amides (12), so these generalities are an over simplification, but the assumptions were used as a first approximation to have a starting point. Because the amide was going to be used as a phase modifier and not as an extracting ligand, it was decided that the ligand's donor properties were least important.

Other factors in the choice of amides was that it have low aqueous solubility, low flammability, reasonable viscosity, and the physical properties required for use as a process solvent. It should also have reasonable hydrolytic and radiolytic stability (9, 12, 13). To obtain this stability, it would need to have long alkyl chains on the amide nitrogen to hinder hydrolysis. It was decided to test two dioctylamine isomers, the di-n-octylamine and the di-2-ethylhexylamine substituents. It was assumed that the branched amide might have a little less third-phase formation because of the steric effects near the carbonyl.

Solubility and Third-phase Formation Testing. All amides tested appeared to be completely miscible with dodecane. Several other solvents were evaluated including cyclohexane, n-octane, 2,2,4-trimethylpentane, n-decane, 1,4-diisopropylbenzene, Isopar H and TPH. The results upon contact with various concentrations of nitric acid in the above solvents are reported in Figures 3, 4 and 5. The amide solutions were shaken for several minutes and centrifuged for rapid phase disengagement. Observation as to the formation of a third phase was made.

It can be seen in Figure 3 that third-phase formation for C-14 alkylmalonamide (compound III) is solvent dependent. Aromatic-type solvents such as diisopropylbenzene (DIPB) reduced third-phase formation. Among the

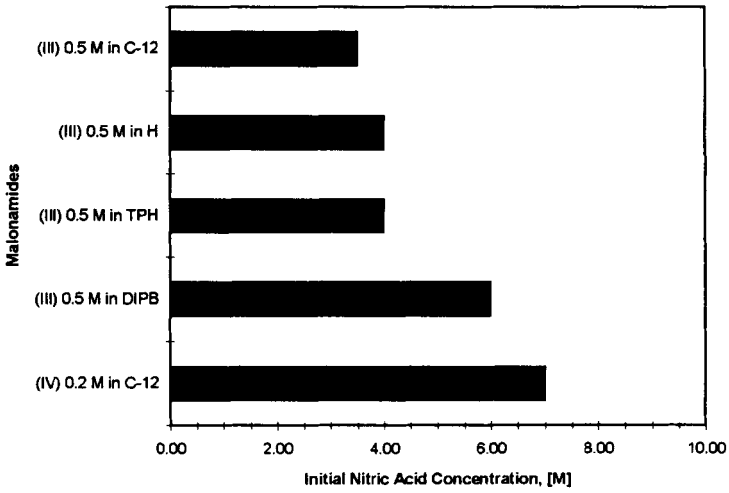

FIGURE 3. Effect of nitric acid concentration on third-phase formation of C-14 and C-20 malonamides.

Symbols for Figures 3 through 5

Compounds:

III. C-14 malonamide ($C_{27}H_{54}N_2O_2$)
IV. C-20 malonamide ($C_{33}H_{66}N_2O_2$)
V. N,N-methylbutylnonanamide
VI. N,N-dioctylacetamide)
VII. N,N-di(2-ethylhexyl)acetamide
VIII. N,N-diethyldodecanamide(comm.)

Solvents:

C-12 n-dodecane
C-10 n-decane
TMP 2,2,4- trimethylpentane
C-8 n-octane
C-6 cyclohexane
DIPB 1,4-diisopropylbenzene
H Isopar H, isoparaffinic hydrocarbon blend
TPH hydrogenated tetrapropylene

Note: Bar graphs show highest concentration at which no third phase was observed in 0.5 M acid increments.

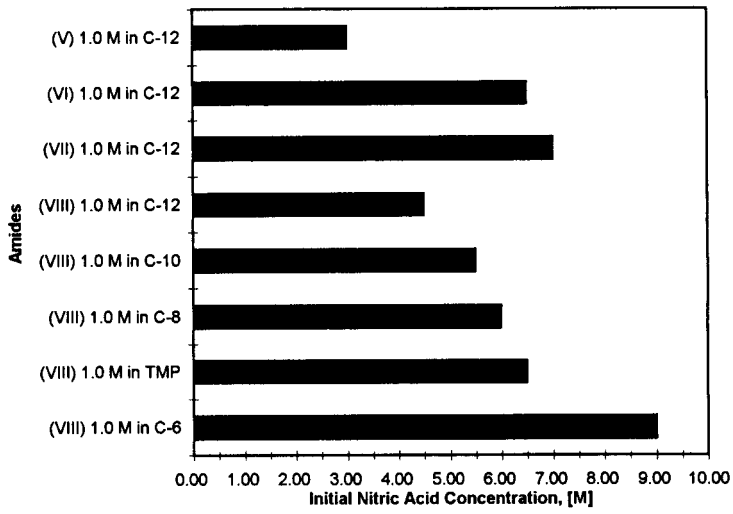

FIGURE 4. Effect of nitric acid concentration on third-phase formation of amides.

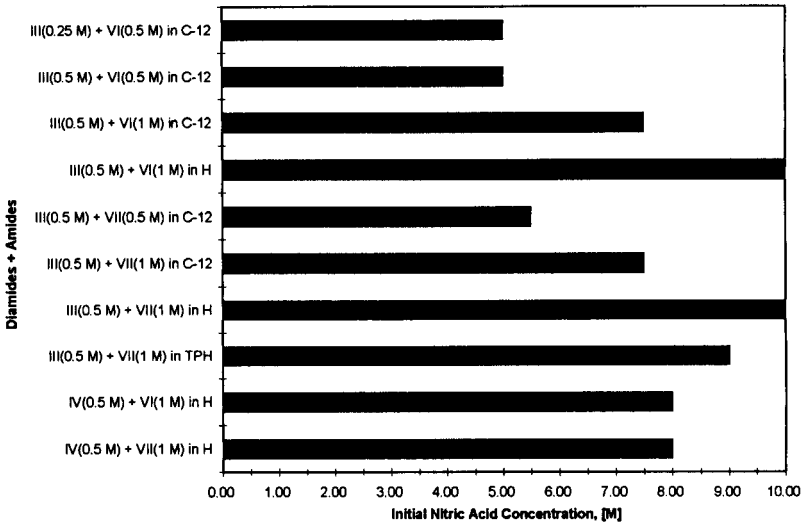

FIGURE 5. Effect of nitric acid concentration on third-phase formation of C-14, C-20 malonamides with amide phase modifiers.

paraffinic hydrocarbons, the branched solvents reduced third-phase more relative to unbranched solvents.

Figure 4 shows solubilities of the amides being evaluated in a variety of solvents. Both the acetamides (compound VI and VII at 1.0 M) were similar in behavior and neither formed a third phase until greater than 6.5 M nitric acid was reached in dodecane solvent. The slight difference between the concentrations of nitric acid at which the third phase formed (7 M for N,N-dioctylacetamide, 7.5 M for N,N-di(2-ethylhexyl)acetamide) could be accounted for by the difference in dipole moments and/or basicity. The other two amides (at 1.0 M), N,N-methyl-n-butylnonanamide and N,N-diethyldodecanamide, gave third phases at 3.5 M and 5.0 M HNO_3, respectively in dodecane solvent. The data shows that the better phase modifiers are those amides with a methyl group attached to the carbonyl and long alkyl chains on the nitrogen, the acetamides, perhaps because they are less likely to form protonated complexes (are less basic) and therefore would be less likely to form a third phase. The acetamides may have a higher dipole moment than the other amides studied, which could also account for their better phase-modifying properties.

There is a correlation between boiling point and third phase formation; the lower the boiling point of the solvent, the less the formation of the third phase. Solvents such as n-octane, though, which give reduced third-phase formation, are not suitable as process solvents because their flash points are too low (for example, n-octane, Fp = 60°F(15°C)). There was a small difference as to third-phase reduction between the branched and normal octane (6.5 M as opposed to 6.0 M, respectively), but the cyclohexane greatly reduced the third phase (nitric acid was 9.0 M before a third phase formed). This showed the correlation between solvent branching and third-phase formation; the greater the branching in the solvent, the higher the HNO_3 concentration necessary before a third phase formed.

The two acetamides (compounds VI and VII) were chosen for further testing with the alkylmalonamide (compound III) because they showed the best overall performance of the four amides. Figure 5 gives the results of mixing 1 M amide with the 0.5 M alkylmalonamide in several different solvents. The alkylmalonamide in dodecane formed a third phase at 4.0 M HNO_3 without the amide phase

modifier. When the two acetamide modifiers were added, the dodecane solution did not form a third phase until exposed to 8.0 M HNO_3 for both amide modifiers. Thus, third-phase formation was reduced and the acid working range extended for the C-14 alkylmalonamide from 3.5 M acid to 7.5 M acid in dodecane solvent. The C-14 malonamide (compound III)/acetamide (compounds VI, VII) mixtures in Isopar H showed no third phase formation even at 10 M HNO_3 extending the working range from 4 M acid to greater than 10 M acid. The C-14 malonamide (compound III)/acetamide (compound VII) mixtures in TPH solvent extended the working range to 9 M HNO_3 from 4 M acid, less than for Isopar H. Comparison of the two high-boiling, branched solvents, (Isopar H and TPH) showed that the higher the boiling point range of the material, the greater the tendency toward third-phase formation (Isopar H is a blend of C_9 to C_{12} isoparaffinic hyrdocarbons). GC analysis of these two high boiling, branched solvents indicated that TPH has a greater proportion of higher boiling material than Isopar H, even though both solvents have a flash point greater than 170° F. (Hewlett-Packard Model 5890A, HP-5 column, 25M, 0.2-mm bore, 0.32-μm coating; initial temperature = 50°C, final temperature = 100°C, rate = 2°C/min; Isopar H retention times from 6.61 to 13.12 minutes, TPH retention times from 7.24 to 16.23 min). Further refinements were made on the system. It was determined that when the amount of phase modifier (compounds VI and VII) was reduced from 1 M to 0.5 M, that the acid working range could still be extended from 3.0 M to 5.5 M before third-phase formation occured in dodecane solvent. This reduced use of the phase modifier represents a savings.

The C-20 malonamide/acetamide mixtures in Isopar H showed no third phase at 8 M HNO_3, but the C-20 malonamide is only soluble to about 0.2 M, thus there can not be a direct comparison between the two alkylmalonamides.

Temperature effects on third-phase formation (20, 21, 22). The effect of temperature on third-phase formation was determined. A sample of alkylmalonamide (compound III) in Isopar H was contacted with 4.5 M HNO_3. Under these conditions and at room temperature (≅ 23°C), a large third-phase was observed, indicating that the middle phase was about to disperse and merge into only one

organic phase if there were minor perturbations on the system (e.g., lower acid concentration, etc.). When the sample was heated to 30°C and above, the middle third-phase disappeared. Upon cooling to lower temperatures (e.g., ≤25°C), the third-phase became more persistent. The results are plotted in Figure 6.

The effect of temperature and acid concentration together on third-phase formation were also determined. When only the alkylmalonamide (0.5 M, compound III) was tested for temperature and acid concentration effects in TPH, third-phase formation was observed in all acid concentrations at 5.5°C and 15°C. At 50°C a third phase was still present in the 6.0 M acid sample (Figure 7).

When the alkylmalonamide (0.5 M, compound III) was tested for temperature and acid concentration effects in the presence of the acetamide (compound VII, 0.5 M) phase modifier in dodecane, no third-phase was observed even when the temperature was lowered to 5.5°C in contact with 4 M HNO_3. At 40°C there was no third-phase left in any of the samples (Figure 8).

When the alkylmalonamide (0.5 M, compound III) was tested for temperature and acid concentration effects in the presence of the acetamide phase modifier (compound VII, 1 M) in TPH and with high acid concentrations, there was no third-phase in the 9 M acid samples at 23°C, 30°C, 40°C, and in the 9.5 M sample at 40°C. In all cases when the third phase was close to being destabilized, there was a sudden increase in its size over a small change in either acid concentration or temperature.

A sample of the alkylmalonamide in dodecane (0.5 M) and exposed to 2.5 M nitric acid was cooled below 5.5°C in the freezer without the formation of a third-phase. In all probability there is a lower acid limit below which a third-phase cannot be induced.

Jenkins and Wain have shown with amine ligands that this solubility effect is from an increase in solubility of the acid-amine complex, rather than a decrease in distribution of the free acid with temperature (20). Possibly the same effect is active with malonamides/amide systems.

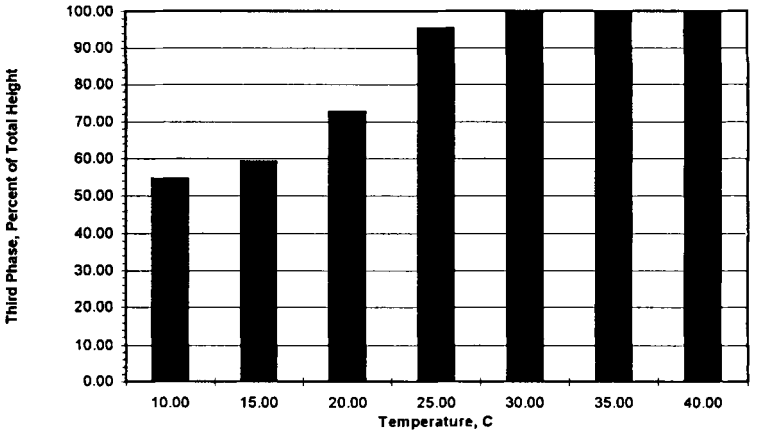

FIGURE 6. Temperature effect on third-phase: 0.5 M compound III in Isopar H/4.5 M nitric acid.

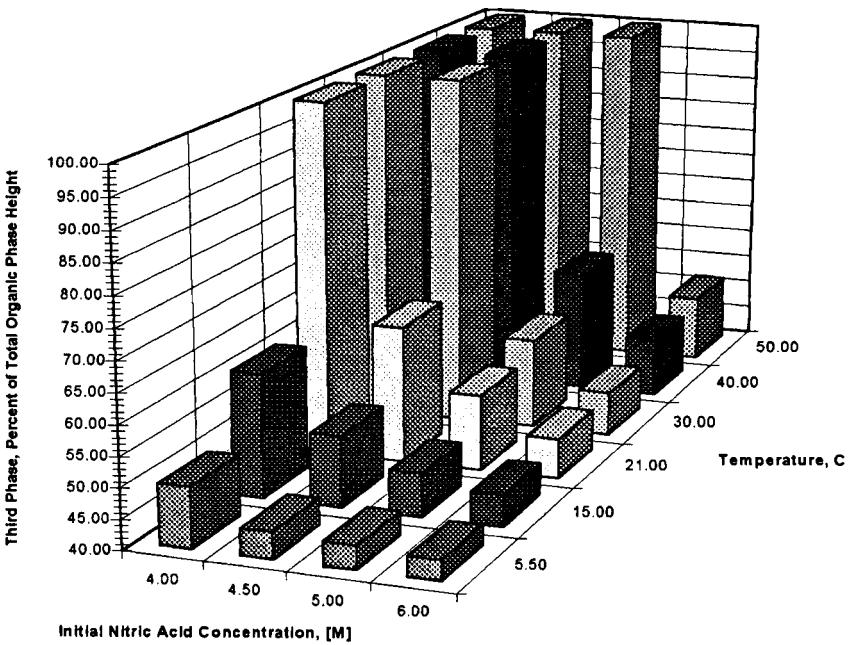

FIGURE 7. Effect of nitric acid concentration and temperature on third-phase size, 0.5 M C-14 in TPH.

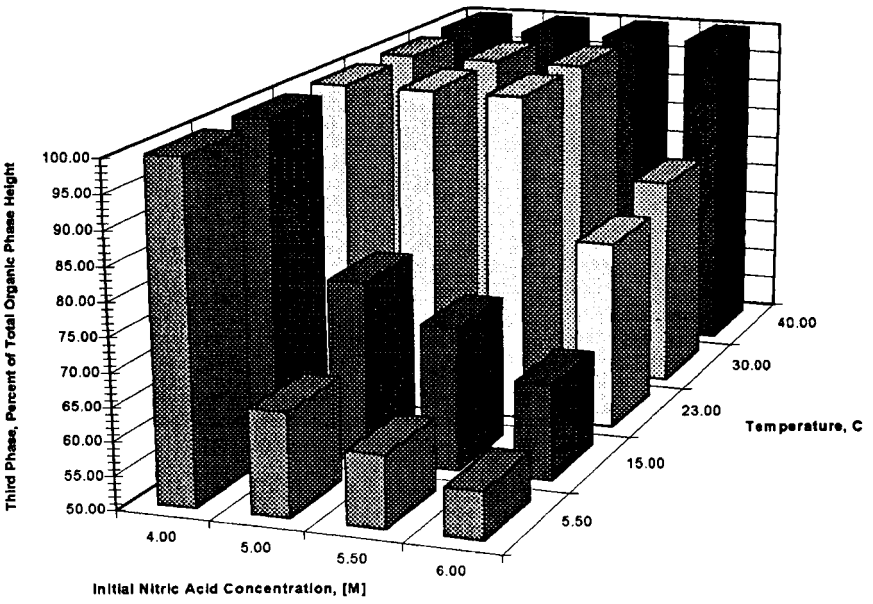

FIGURE 8. Effect of nitric acid concentration and temperature on third-phase size, 0.5 M C-14 + 0.5 M DEHAA in dodecane.

K_d Determinations of Am for Modified Solvent System. Once our goal of reducing the third-phase formation was achieved, we needed to determine the effect of the phase modifier on the overall extraction capability of the system for americium and europium. Figure 9 gives a plot of K_d versus the initial nitric acid concentration for a variety of solvent systems. It can be seen that the K_d values are at a maximum near 5 M and 6 M acid. The study was maintained below 4 M nitric acid to avoid the third phase in the phase-unmodified system. The distribution value of the phase-modified system is quite comparable to the system without phase modifier. The alkylmalonamide in 1,4-diisopropylbenzene is plotted for comparison; there is no third-phase formation problem in DIPB. There is a small difference in the K_d values between the two acetamide phase modifiers. The branched system, N,N-di(2-ethylhexyl)acetamide (compound VII), gives greater extraction [K_d (dodecane)

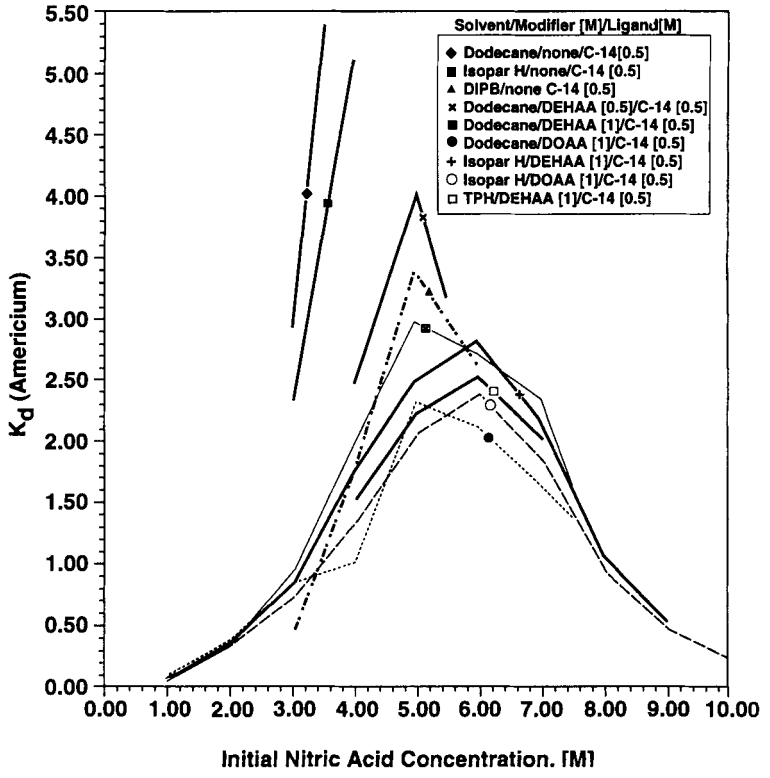

FIGURE 9. Effect of nitric acid concentration on K_d.

= 2.98 (5 M), K_d (Isopar H) = 2.81 (6 M)] than the unbranched amide, N,N-dioctylacetamide (compound VI) [K_d (dodecane) = 2.29 (5 M), K_d (Isopar H) = 2.35 (6 M)].

The K_d values for americium were highest when there was no phase modifier present in the unbranched solvent; dodecane was slightly better than Isopar H. However, third-phase formation occurred at 4 M HNO_3 with the dodecane solvent, so it is difficult to determine the extraction maximum as a function of acid concentration. The extraction maximum occurred at 5 M nitric acid for the phase-modified dodecane system and at 6 M acid for the phase-modified

Isopar H system. It is interesting that with the phase-modified system, dodecane/DEHAA, the highest K_d value of all the phase-modified systems was realized. It is curious that a branched phase modifier worked best with an unbranched solvent. Thus, the balance between optimizing K_d values and minimizing third-phase formation was reached by using an unbranched solvent, dodecane, to raise the K_d values, and a branched acetamide, DEHAA, to optimally reduce third-phase formation up to 8 M HNO_3.

Since the extraction maximum for americium is about 5 M acid, the need to work at much higher acid concentrations is not necessary. Working at higher acid concentrations under highly radiolytic fields increases the chances of solvent degradation from radiolysis and hydrolysis. To take the optimization process further, we reduced the amount of modifier to 0.5 M to determine if the K_d values could be increased even more and if the third-phase formation would remain suppressed. As shown in figure 9, this solvent system does give the best K_d value (4.0) at 5.0 M HNO_3 of all the phase-modified systems studied (better than DIPB, K_d = 3.4 at 5.0 M HNO_3, the next best solvent without third-phase formation problems).

The effect on separation factors between Am and Eu were tested with the optimum conditions of alkylmalonamide (compound III) and amide (compound VII) in dodecane and compound III alone in dodecane and Isopar H. The results are presented in Table 1. From the data of the alkylmalonamide in Isopar H and dodecane it can be seen that the solvent has little effect on the separation factors. It is interesting that Am is favored over Eu in the amide/malonamide system when compared to the organophosphorous bidentate system of CMPO/TBP or CMP/TBP. This has been observed before with the malonamide extractants.

The optimal system was also tested loaded with 0.025 M europium (from europium nitrate hexahydrate) or 0.025 M uranyl (from uranyl nitrate hexahydrate) in 5.0 M HNO_3. The results are reported in Table 2. The separation factor is similar to the unloaded system in Table 1 (optimal system - 5 M HNO_3), but the americium and europium K_d values were low, though, still greater than 1. No third phase occurred in either sample at room temperature.

TABLE 1. EFFECT OF SOLVENT, NITRIC ACID CONCENTRATION, AND PRESENCE OF MODIFIER ON K_d'S AND SEPARATION FACTORS FOR AM AND EU

Solvent	HNO_3 Conc.	Monamide Conc. [M]	Diamide Conc. [M]	Average K_d Eu	Average K_d Am	Average SF K_d Am/Kd Eu
Dodecane	5.00	0.50 (DEHAA)	0.50	2.59	3.74	1.45
Dodecane	3.00	0	0.50	1.40	2.56	1.82
Dodecane	3.50	0	0.50	2.52	3.38	1.34
Isopar H	3.00	0	0.50	1.30	2.31	1.78
Isopar H	4.00	0	0.50	3.50	4.64	1.33

average of two tests.

TABLE 2. EFFECT OF URANIUM AND EUROPIUM LOADING ON K_d'S VALUES AND SEPARATION FACTORS FOR AM AND EU

Metal	Solvent	HNO_3 Conc.	Monamide Conc. [M]	Diamide Conc. [M]	K_d Eu	K_d Am	SF K_d Am/ K_d Eu
Uranium	Dodecane	5.00	0.50 (DEHAA)	0.50	1.87	2.78	1.49
Europium	Dodecane	5.00	0.50 (DEHAA)	0.50	1.60	2.28	1.42

CONCLUSIONS

We have developed an improved synthetic procedure for the alkylmalonamide ligands which avoids the use of expensive and highly reactive reagents. The new alkylmalonamide with the C-20 chain proved to be less useful for extraction as it had half the solubility of the C-14 alkylmalonamide in dodecane and reduced solubility in isopar H.

We have developed a phase modification system that extends the working process range of the alkylmalonamides in dodecane from 3.5 M to 7.5 M nitric acid and in Isopar H from 4.0 M to 10.0 M nitric acid. The resulting K_d values are comparable to Isopar H and TPH solvent, but the phase-modified system is more robust, showing less sensitivity to temperature and acid concentration effects compared to the phase-unmodified system.

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