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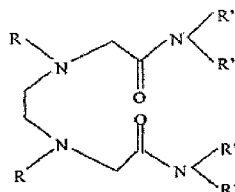
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(54) **Title:** DIALKYLDIAZA-TETRAALKYLOCTANE DIAMIDE DERIVATIVES USEFUL FOR THE SEPARATION OF TRIVALENT ACTINIDES FROM LANTHANIDES AND PROCESS FOR THE PREPARATION THEREOF



(1)

(57) **Abstract:** The novel lipophilic metal extractants of the class dialkyl-diaza-tetraalkyloctanediamide (DADA) useful to selectively separate trivalent americium (sup. 241 Am) from trivalent lanthanides are represented by the formula (1): Wherein R is a C₁ to C₅ normal alkyl and R' is a C₄ to C₈ normal and branched alkyl group. The compounds are synthesized at high yield and purity by the reaction of corresponding N,N'-dialkylethylenediamine and N,N'-dialkyl-2-chloroacetamide. The separation is achieved by utilizing the soft-soft interaction between the trivalent actinides and 'N' atoms of the extractant. Both soft donor 'n' and hard donor 'O' sites are incorporated in the molecule for better extraction of trivalent actinides over trivalent lanthanides. Thus, this molecule can be used as selective extractant to separate trivalent actinides from trivalent lanthanides.

**DIALKYLDIAZA-TETRAALKYLOCTANE DIAMIDE DERIVATIVES USEFUL FOR
THE SEPARATION OF TRIVALENT ACTINIDES FROM LANTHANIDES
AND PROCESS FOR THE PREPARATION THEREOF**

Field of the invention

The present invention relates to a novel lipophilic extractant, its preparation process and its use in selective separation of trivalent actinides from lanthanides.

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More particularly, the present invention relates to a novel lipophilic extractant of the class dialkyldiaza-tetraalkyloctanediamides, for the separation of trace concentration of trivalent americium (^{241}Am) from macro amount of trivalent lanthanides from aqueous radioactive waste streams.

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Background and prior art

Reprocessing of spent fuel by the PUREX process leads to generation of high-level liquid waste (HLLW). Presences of the long-lived minor actinides in the waste essentially determine its long-term hazard potential. Keeping in view of the long-term strategy for the management of the waste, it is desirable that the waste be subjected to partitioning to devoid the actinides from HLLW. This technology will pave the way for subjecting the actinides either to transmutation or immobilizing them in suitable host materials for their long term management.

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The presently known processes as TRUEX, DIAMEX and solvents such as TRPO, diglycolamides made it possible to extract trivalent actinides in organic solvents from HLLW. But in all these processes trivalent lanthanides resulting from the fission were also extracted along with actinides in the organic phase. The back extraction of the organic phase results in the aqueous phase containing both the trivalent actinides and lanthanides. However, in order to further improve the control of waste materials, it would be of vital interest to separate minor actinides from lanthanides. Accordingly, efficient separation processes continue to be sought, and this is the context in which most current researches on ligand design were being carried out.

Group separation of trivalent actinides from lanthanides is difficult because they tend to form similar coordination complexes with ligands due to their similar charge densities. These separations however, can be accomplished by utilizing the fact that a small degree of covalency in the bond between actinide-ligands exists over
5 lanthanide ligands. The increased covalency results in actinide elements having slightly higher affinity for soft donor ligands having N and S donor atoms. Using this principle various extractants have been developed.

The sulphur containing extractants like dithiophosphoric acid, bis (2,4,4,trimethyl
10 pentyl) dithiophosphinic acid and bis(dichlorophenyl) dithiophosphinic acid are described by C. Musikas, G. Le Marios, R. Fitoussi and C. Cuillerdier, Actinide separations, ACS Symposium Series, Vol.117,1980; R. Fitoussi, C.Musikas, US Patent 4461747; Y.Zhu, Radiochimica Acta, 68, 95-98, 1995; Y.Zhu, J.Chen and Rongzhou Jiao, Solv.Extr. Ion Exch. 14(1), 61-68, 1996; G. Modolo, R.Odoj. Solv.
15 Extr. Ion. Exch., 17 (1), 33-53, 1999. However, their susceptibility to degradation under process conditions limits their use.

Nitrogen containing extractants like TPTZ, nPr-BTP, and TPEN are described by M.Bonnin, C.Musikas, P.Vitorge, U.S. Patent, 4,496,523, 1985; Z.Kolarik, U. Mullich,
20 F.Gassener, Solv. Extr. Ion Exch., 17(5), 1155-1170, 1999; T. Matsumura and K. Takeshita, J. Nuc, Sci. Tech., 43,7,824-827, nPr-BTP and their derivatives are superior in selectivity and efficiency, however their performance is reduced due to degradation during practical use. TPTZ and TPEN alone have weak interaction with trivalent actinides and used in a synergistic combination with a lipophilic cation
25 exchanger having hard donor oxygen atom for better extractability.

Thus there is a need to provide an extractant, which overcomes the problems of the compounds as taught in the prior art.

The present inventors have found that the subject compounds of the present invention differ entirely by their chemical structure where both soft donor nitrogen atoms and hard donor oxygen atoms are incorporated in the molecule to attain the separation without use of second extracting agent. The numbers and positions of donor atoms in the molecule are appropriately integrated in order to meet the requirements of favorable complex formation with trivalent actinides over lanthanides.

Objects of the invention

It is an object of the present invention to overcome the drawbacks of the prior art.

It is another object of the present invention to provide a novel lipophilic extractant for separation of trivalent actinides from lanthanides.

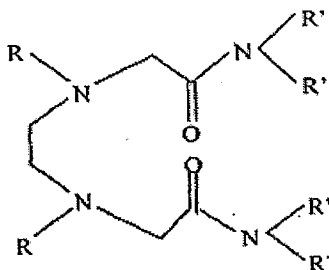
Another object of the present invention is to provide a novel lipophilic extractant for separation of traces concentration of trivalent americium (^{241}Am) from macro amount of trivalent lanthanides from aqueous radioactive waste streams.

Yet another object of the present invention is to provide a process for the preparation of the novel lipophilic extractant.

Summary of the invention

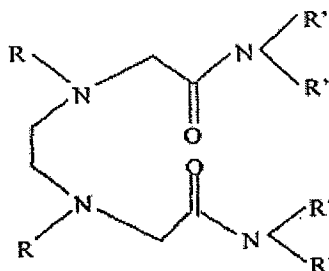
Accordingly, the present invention relates to a lipophilic extractant capable of selectively extracting trivalent actinides from lanthanide ions, represented by the following structural formula 1,

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wherein R is a C₁ to C₅ normal alkyl and R' is a C₄ to C₈ normal and branched alkyl group.

Another aspect of the present invention is to provide A process for the preparation of lipophilic extractant of formula 1,



wherein R is a C₁ to C₅ normal alkyl and R' is a C₄ to C₈ normal and branched alkyl group

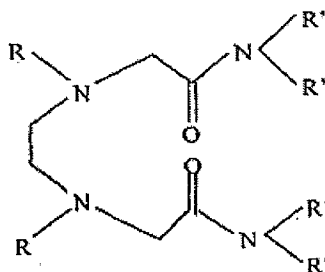
wherein said process comprises the steps of:

- (i) condensing one mole of N, N'-dialkylethylenediamine of the structural formula 2 with 2.2 to 5.0 moles of N,N-dialkyl-2-chloroacetamide of the structural formula 3 in the presence of 2.2 to 10 moles of triethylamine.
- (ii) diluting the reaction mixture with xylene and neutralizing with 1.0M hydrochloric acid;

- (iii) separation of the organic phase and washing with water and 2.0% sodium carbonate solution and further washed with water to neutral pH.
- (iv) drying the organic phase with anhydrous sodium sulphate and concentrated by distillation under reduced pressure.
- (v) distillation of the residue at 120°C under vacuum of about 1.0 millitorr using centrifugal molecular distillation unit to remove the unreacted N,N-dialkyl-2-chloroacetamide.
- (vi) obtaining the product as residue having a purity of about 96%.
- (vii) Characterization of the compound by elemental analyzer, GC-MS and NMR.

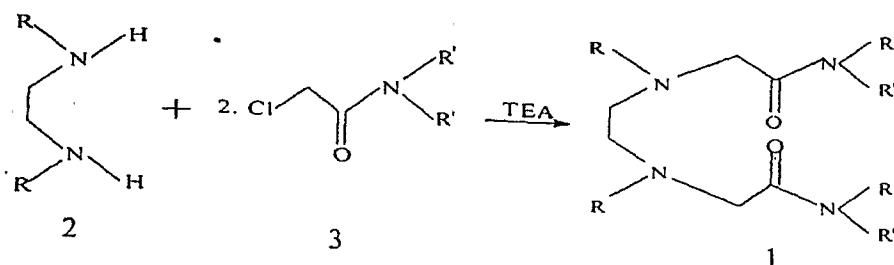
Detail description of the invention

Accordingly, the present invention to a novel lipophilic extractant of the class dialkyldiaza-tetraalkyloctanediamides and the preparation of the compound of structural formula 1:



According to the present invention, the novel lipophilic extractant is prepared by the following process comprising the steps of condensing One mole of N, N'-dialkylethylenediamine of the structural formula 2 with 2.2 to 5.0 moles of N,N-dialkyl-2-chloroacetamide of the structural formula 3, in the presence of 2.2 to 10 moles of triethylamine. The reaction was carried out at 60-85°C for 48 hrs in N₂ atmosphere. The overall synthesis scheme is shown as under:

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On cooling the reaction mixture is diluted with xylene and neutralized with 1.0M hydrochloric acid. The organic phase is separated and washed with water and 2.0% sodium carbonate solution and further washed with water to neutral pH. The organic phase is dried with anhydrous sodium sulphate and concentrated by distillation under reduced pressure. The residue is further distilled at 120°C under vacuum of about 1.0 millitorr using centrifugal molecular distillation unit to remove the unreacted N, N-dialkyl-2-chloroacetamide. The product obtained as residue is having a purity of about 96%. The overall yield of the process was about 40 to 90%. The compound is characterized by elemental analyzer, GC-MS and NMR.

The compounds of the structural formula 2 and formula 3 are prepared as per procedure given in Beil.6 (4), 3529 and Solv. Extr. Ion Exch., 5,6,1075 (1987) respectively.

The exemplary compounds of structural formula 1, synthesized in this invention are as under :

- N,N,N',N' – tetra isobutyl-3,6 (N'', N''' dimethyl) diaza-octane 1, 8 diamide;
- N,N,N',N' – tetra hexyl-3,6 (N'', N''' dimethyl) diaza-octane 1,8 diamide;
- N,N,N',N' – tetra (2-ethylhexyl)-3, 6 (N'', N''' dimethyl) diaza-octane 1, 8 diamide;
- N,N,N',N' – tetra isobutyl-3,6 (N'', N''' diethyl) diaza-octane 1,8, diamide;

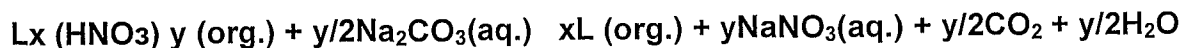
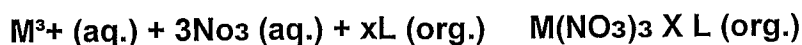
- N,N,N',N' – tetra hexyl-3, 6 (N'', N''' diethyl) diaza-octane 1, 8 diamide;
 N,N,N',N' – tetra (2-ethylhexyl)-3,6 (N'', N''' diethyl) diaza-octane 1, 8 diamide;
 N,N,N',N' – tetra isobutyl-3,6 (N'', N''' dipropyl) diaza-octane 1, 8 diamide;
 N,N,N',N' – tetra hexyl-3,6 (N'', N''' dipropyl) diaza-octane 1, 8 diamide;
 5 N,N,N',N' – tetra (2-ethylhexyl)-3,6 (N'', N''' dipropyl) diaza-octane 1,8 diamide;
 N,N,N',N' – tetra isobutyl-3,6 (N'', N''' dibutyl) diaza-octane 1, 8 diamide;
 N,N,N',N' – tetra hexyl-3,6 (N'', N''' dibutyl) diaza-octane 1, 8 diamide;
 N,N,N',N' – tetra (2-ethylhexyl)-3,6 (N'', N''' dibutyl) diaza-octane 1,8 diamide;
 N,N,N',N' – tetra isobutyl 1-3, 6(N'', N''' dipentyl) diaza-octane 1, 8 diamide;
 10 N,N,N',N' – tetra hexyl-3,6 (N'', N''' dipentyl) diaza-octane 1, 8 diamide;
 N,N,N',N' – tetra (2-ethylhexyl)-3,6 (N'', N''' dipentyl) diaza-octane 1, 8 diamide.

- Among these, the most preferred compounds are N,N,N',N' – tetra (2-ethylhexyl)-3,6 (N'', N''' dibutyl) diaza-octane 1,8 diamide and N,N,N',N'-tetra (2-ethylhexyl)-3,6
 15 (N'', N''' dipentyl) diaza-octane 1, 8 diamide. The lower alkyl derivatives of diazadiamide $R=C_1$ to C_3 and R' =isobutyl and hexyl, are found to be either hydrophilic in nature or have excessive tendency to form crud in acidic medium. Therefore, during various steps of synthesis and workup, they could not be obtained in better yields. The higher homologues of diaza-diamide, where R is C_6 and above
 20 could not be synthesized in better yields under the similar conditions of reactions. This could be due to large steric hindrance and electronic effect imparted by alkyl group of ethylenediamine moiety which slows down the condensation with amidic moiety.
- 25 The preferred compounds have desirable lipophilicity to use it as extractant and diluted in 1-octanol for its effective use. The concentration of 0.1M extractant in 1-octanol was found to be optimum for achieving the workable separation between trivalent actinides and lanthanides.

The extraction is performed by contacting aqueous phase containing both trivalent actinides and lanthanides with organic phase at the phase ratio of 1:1. After agitation for 30 minutes and separation of two phases, the metal ion content of each phase is measured to determine the distribution co-efficient of each of metal ions. All the extraction experiments are performed at ambient conditions of temperature and pressure. The concentration of americium was determined by gamma spectrometry and lanthanides (Ln's) by ICP---AES analysis.

The distribution coefficient D_M of a metal is determined as a ratio of concentration of the metal in the organic phase to the aqueous phase. The separation factor is calculated by determining D_{Am} and D_{Ln} 's in the presence of each other and defined as D_{Am}/D_{Ln} 's.

Maximum extraction is obtained in the pH range of 2.0 to 3.0 Complete stripping of the actinide from the loaded organic phase was achieved using 0.5M nitric acid. During the stripping process nitric acid replaces the actinide nitrate from the complex. The reuse of the solvent is done by neutralizing the solvent with 2.0% sodium carbonate solution. The extraction, stripping and reuse of the solvent are shown by the following equations :



A better understanding of the present invention can be obtained from the study of the following illustrative and non-limitative examples.

Example 1**Synthesis of N, N, N', N' – tetra (2-ethylhexyl)-3, 6 (N'', N''' dibutyl) diaza-octane 1,8 diamide**

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209 ml (1.0 mol) of N, N' – dibutylethylenediamine, 785 ml (2.45 mol) of N, N-(2-ethylhexyl)-2-chloroacetamide and 900 ml (6.45 mol) of triethylamine are mixed together and well stirred at room temperature under nitrogen atmosphere. The temperature of the reaction mixture is slowly raised and refluxed at 85°C for 48 hours under vigorous stirring. The progress of the reaction was monitored by GC-MS. On cooling the reaction mixture is diluted with xylene and neutralized with 1.0M hydrochloric acid. The organic phase is separated and washed with water and 2.0% sodium carbonate solution and further washed with water to neutral pH. The organic is dried with anhydrous sodium sulphate and concentrated by distillation under reduced pressure. The residue is further distilled at 140°C under vacuum of about 1.0 millitorr using centrifugal molecular distillation unit to remove the unreacted N, N-(2-ethylhexyl)-2-chloroacetamide almost completely. The product obtained as thick viscous oily residue is having a purity of about 96% (GC-MS). The overall yield of the process is about 90%. The compound is characterized by elemental analyzer, GC-MS and NMR.

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GC-MS is performed on Shimadzu GCMS-QP2010 plus instrument with a single quadrupole mass spectrometer at 70eV using 10m X 0.25 mm CP-Sil5CB fused silica capillary column. Helium is the carrier and the temperature program was 60°C for 1 minute, increased at 280°C at 10°C per minute and held at 280°C for 20 minutes. The injector temperature was 300°C.

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GC-MS: 10.79 min., 0.76%, m/z 318 calculated for ClCH₂CON(C₈H₁₇)₂; 12.88 min., 0.47%, m/z 354 calculated for (C₄H₉)NHCH₂CON (C₈H₁₇)₂; 20.184 min.,

2.36%, m/z 635 calculated for C₈H₁₇)₂NC(O)CH₂N(C₄H₉)(CH₂)₂N(C₄H₉)CH₂C(O)N(CH₃)C₈H₁₇; 22.59 min., 96.10%, m/z 734 calculated for (C₈H₁₇)₂ NC(O) CH₂N(C₄H₉) (CH₂)₂ N (C₄H₉) – CH₂C (O)N (C₈H₁₇)₂.

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Elemental analysis for C₄₆H₉₄O₂N₄

Calculated : C, 75.14; H, 12.88; O, 4.35; N, 7.61

Found :C, 75.28; H, 12.80;), 4.23; N, 7.69

- 10 NMR spectra of DADA appropriately dissolved in CDCl₃ are measured on a Bruker AV 500 spectrometer at 500 MHz with TMS as an internal reference.

Nuclear magnetic resonance spectra of proton has shown a singlet peak over 3.644-3.541 ppm for four protons of two methylene groups, multiplet peak over 3.283-3.166 ppm for eight protons of two – NCH₂CH₂ - groups, singlet peak over 2.977-2.895 ppm for four protons of – NCH₂CH₂N – group, multiplet over 1.627 – 1.464 ppm for eight protons of four – CO-N-CH₂ - groups, multiplet over 1.351 – 1.120 ppm for forty protons of four – CH(C₂H₅)CH₂-CH₂ - groups and the multiplet peak over 0.872 – 0.818 ppm for thirty protons of six – CH₂CH₃ groups.

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¹³C NMR : 169.0 ppm for C=O group, 77.641 – 76.364 ppm for – CH₂- of – N-CH₂-CO-, 55.158, 52.022, 50.023, 47.706 ppm for – N-C of amidic group, 37.562, 36.217 ppm for – N-CH₂-CH₂-N-, 30.089, 28.230 ppm for –N-CH₂-23.352, 22.662, 22.597, 19.594, 13.625, 10.567 and 10.108 ppm for rest of the – CH₂-CH₂-and –CH₂-CH₃.

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Example II to VI

The procedure of example 1 was repeated for synthesis of various diazaoctanediamides where a given N, N' – dialkylethylenediamine is reacted with different alkyl substituted chloroacetamide. They are indicated in Table 1,

Table 1

Sr. No.	Example	N,N' dialkylethylenediamine Alkyl	N,N,diakyl-2-chloroacetamide Alkyl
1	II	Methyl	a. isobutyl b. hexyl c. 2-ethylhexyl
2	III	Ethyl	a. isobutyl b. hexyl c. 2-ethylhexyl
3	IV	Propyl	a. isobutyl b. hexyl c. 2-ethylhexyl
4	V	Butyl	a. isobutyl b. hexyl c. 2-ethylhexyl
5	VI	Pentyl	a. isobutyl b. hexyl c. 2-ethylhexyl

5 EXAMPLE VII

In this example, use is made as the solvent formed by dissolving N, N, N', N' – tetra (2-ethylhexyl) 3,6 – (N'', N''' dibutyl)diaza-octane 1,8 diamide in 1-octanol to a concentration of 0.1M.

- 10 To perform extraction, this organic solvent is brought into contact with nitric acid solution at pH 2.5 containing 1 mg/l Am, 50 mg/l Eu, 200 mg/l La, 200 mg/l Ce,

0.25 M NaNO₃. After agitation for 30 minutes, and the decantation of two phases, the americium and lanthanides content of each phase is measured to determine the distribution co-efficients and separation factors. All experiments are carried out at aqueous to organic phase ratio of one and at ambient conditions.

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Table 2 shows the results of the extraction studies.

Table 2

Sr. No.	Elements	Distribution co-efficient DM	Separation Factor (DAm/DLn's)
1	Am	1.58	
2.	Eu	0.13	????
			12.15
3.	Ce	0.333	47.87
4.	La	0.023	68.70

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The other preferred compound namely N,N,N',N' – tetra (2-ethylhexyl) 3,6-(N'', N''' dipentyl) diaza-octane 1,8 diamide has shown similar extraction behaviour.

On the basis of these results, it can be seen that the extractants of present invention can be a suitable ingredient for the separation of trivalent actinides from lanthanides.

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Reference	Extraction of....	Extractant with soft donor (prior art) (Nitrogen donor)	Extractant with hard donor (prior art) (Oxygen donor)
M.Bonnin, C.Musikas, P.Vitorge (US Patent 4496523) Fig.1	Am(III) At 0.117M HNO ₃	0.01M TPTZ / Tert.butyl benzene $D_{Am} = 0.001$ % Extraction = 10^{-4}	0.01M HDNNS / Tert.butyl benzene $D_{Am} = 500$ % Extraction = 99.8
	Eu(III) At 0.117M HNO ₃	TPTZ $D_{Eu} = 0.001$ % Extraction = 10^{-4}	HDNNS $D_{Eu} = 500$ % Extraction = 99.8

Reference	Extraction of....	Extractant with soft donor (prior art) (Sulphur donor)	Extractant with hard donor (prior art) (Oxygen donor)
R. Fitoussi, C.Musikas, (US Patent 4461747) Fig.1	Am(III) At 0.05M HNO ₃	1.0 M HDEHDTP / n-dodecane $D_{Am} = 0.01$ % Extraction < 10^{-2}	1.0M TBP / n-dodecane $D_{Am} = 0.001$ % Extraction = 10^{-4}
	Eu(III) At 0.05M HNO ₃	1.0 M HDEHDTP / n-dodecane $D_{Am} = 0.01$ % Extraction < 10^{-2}	1.0M TBP / n-dodecane $D_{Am} = 0.001$ % Extraction = 10^{-4}

Reference	Extraction of....	Extractant with soft donor (prior art) (Sulphur donor)	Extractant with hard donor (prior art) (Oxygen donor)
G. Modolo, R.Odoj. Solv.Extr. Ion.Exch. 17(1), 33-53, 1999. (Fig.3)	Am(III) At pH = 1.6, 1M NaNO ₃	di(p-chlorophenyl) dithiophosphinic acid/ toluene $D_{Am} < 1.0 \times 10^{-3}$ % Extraction < 10^{-4}	1.0M TBP / n-dodecane $D_{Am} < 1.0 \times 10^{-3}$ % Extraction < 10^{-4}
	Eu(III) At pH = 1.6, 1M NaNO ₃	di(p-chlorophenyl) dithiophosphinic acid/ toluene $D_{Am} < 1.0 \times 10^{-3}$ % Extraction < 10^{-4}	1.0M TBP / n-dodecane $D_{Am} < 1.0 \times 10^{-3}$ % Extraction < 10^{-4}

Note: No separation of Am from Eu is achieved when the above soft donor extractants and hard donor extractants are used independently.

Reference	Extraction of....	Extractant with soft donor (prior art) (Sulphur donor)	Extractant with hard donor (prior art) (Oxygen donor)
Y.Zhu, J.Chen and Rongzhou Jiao Solv.Extr. Ion Exch. 14(1), 61-68, 1996. {Fig.1)	Am(III) At pH = 3.0, 1M NaNO ₃	0.5MCyanex-301/kerosene D _{Am} = 0.4 % Extraction = 28.0	-
	Eu(III) At pH = 4.0, 1M NaNO ₃	0.5MCyanex-301/kerosene D _{Eu} = 0.1 % Extraction = 9.0	-

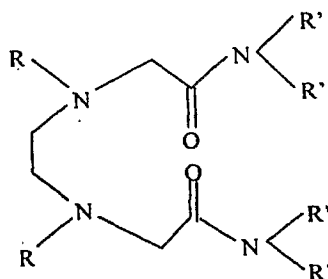
Reference	Extraction of....	Extractant with soft and hard donor Dialkyldiaza tetraalkyloctane- diamides (DADA)
Present Invention	Am and Eu, at 0.25 M NaNO ₃ and pH = 2.5	0.1M DADA/1-octanol D _{Am} = 1.58 % Extraction = 62.0 D _{Eu} = 0.13 % Extraction = 11.4

- 5 Comparison of extraction behavior of the extractants under similar condition and to bring them on a single scale is difficult as different extractants work in different conditions like feed composition, salt concentration, extractant concentration, pH, diluents etc.

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CLAIMS

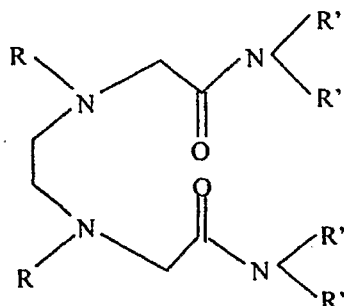
1. A lipophillic extractant capable of selectively extracting trivalent actinides from lanthanide ions, represented by the following structural formula 1:



wherein R is a C₁ to C₅ normal alkyl and R' is a C₄ to C₈ normal and branched alkyl group.

2. The lipophillic extractant as claimed in claim 1, wherein said extractant is a polydentate ligand having alkyl substituted ethylenediamine skeleton with lipophillic amidic groups attached at both the ends.
3. The lipophillic extractant as claimed in claim 1, wherein the said extractant is a dialkyldiaza-tetralkyloctanediamide.
4. A process for the preparation of lipophillic extractant of formula 1,

16



wherein R is a C₁ to C₅ normal alkyl and R' is a C₄ to C₈ normal and branched alkyl group,

wherein said process comprises the steps of:

- (i) condensing one mole of N, N'-dialkylethylenediamine of the structural formula 2 with 2.2 to 5.0 moles of N,N-dialkyl-2-chloroacetamide of the structural formula 3 in the presence of 2.2 to 10 moles of triethylamine.
- (ii) diluting the reaction mixture with xylene and neutralizing with 1.0M hydrochloric acid;
- (iii) separation of the organic phase and washing with water and 2.0% sodium carbonate solution and further washed with water to neutral pH;
- (iv) drying the organic phase with anhydrous sodium sulphate and concentrated by distillation under reduced pressure;
- (v) distillation of the residue at 120°C under vacuum of about 1.0 millitorr using centrifugal molecular distillation unit to remove the unreacted N,N-dialkyl-2-chloroacetamide;
- (vi) obtaining the product as residue having a purity of about 96%;
- (vii) characterization of the compound by elemental analyzer, GC-MS and NMR.

5. The process as claimed in claim 4, being carried out at a temperature of 60-85°C for 48 hrs in N₂ atmosphere.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2009/000499

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C237/06 C22B3/00 C22B59/00 G21C19/46
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C C22B G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BOROWITZ, I.J. ET AL.: "The preparation and properties of neutral diamide ionophores for group IIA metal cations - II", TETRAHEDRON, vol. 40, no. 6, 1984, pages 1009-1016, XP002612609, * abstract page 1011; compound 11 ----- -/--	1-5

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 December 2010

Date of mailing of the international search report

16/12/2010

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INTERNATIONAL SEARCH REPORT

 International application No
 PCT/IN2009/000499

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>READIO, J. ET AL.: "Metal complexes of N,N,N',N'-tetrakis-(n-propyl)-1,2-phenylenedioxydiacetamide and related ligands", J. COORD. CHEM., vol. 11, 1981, pages 135-142, XP009142047, * abstract; figure 1; table II; compound 7</p>	1-5
A	<p>SASAKI AND S TACHIMORI Y: "EXTRACTION OF ACTINIDES(III),(IV), (V), (VI) AND LANTHANIDES(III) BY STRUCTURALLY TAILORED DIAMIDES", SOLVENT EXTRACTION AND ION EXCHANGE, DEKKER, NEW YORK, NY, US, vol. 20, no. 1, 1 January 2002 (2002-01-01), pages 21-34, XP009080173, ISSN: 0736-6299, DOI: DOI:10.1081/SEI-100108822 * abstract page 23; figure 1</p>	1-5
A	<p>SASAKI Y ET AL: "THE NOVEL EXTRACTANTS, DIGLYCOLAMIDES, FOR THE EXTRACTION OF LANTHANIDES AND ACTINIDES IN HNO₃-N-DODECANE SYSTEM", SOLVENT EXTRACTION AND ION EXCHANGE, DEKKER, NEW YORK, NY, US, vol. 19, no. 1, 1 January 2001 (2001-01-01), pages 91-103, XP009080172, ISSN: 0736-6299, DOI: DOI:10.1081/SEI-100001376 * abstract pages 92-93; tables 1,3</p>	1-5
A	<p>FR 2 810 679 A1 (JAPAN ATOMIC ENERGY RES INST [JP]) 28 December 2001 (2001-12-28) * abstract; claims; examples</p>	1-5
A	<p>EP 1 923 473 A1 (UNIV MADRID AUTONOMA [ES]; INST CATALA D INVESTIGACIO QUI [ES]; CT INV) 21 May 2008 (2008-05-21) * abstract; claims; tables 1,2; compounds 12-18</p>	1-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2009/000499

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			JP	2002001007 A	08-01-2002
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