(12) MALAYSIAN PATENT	(11) MY - 163392 - A

(21) **Application No. :** PI 2012005646

(22) **Filing Date :** 01 July 2011

(47) **Date of Publication and Grant :**
15 September 2017

(30) **Priority Data :**
2010-153188; 05/07/10 ;JP

(51) **Classification, INT CL(2006.01) :**
C07C 231/02
C07C 235/06
C22B 3/26
C22B 7/00
C22B 59/00

(56) **Prior Art :**
JP 2007-327085 A
JP 54-46719 A

(72) **Inventors :**
SAKAKI Kazuaki
SUGAHARA Hiroto
KUME Tetsuya
OHASHI Masaki
NAGANAWA Hirochika
SHIMOJO Kojiro

(73) **Patent Owner :**
1) Shin-Etsu Chemical Co., Ltd.
6-1, Ohtemachi 2-chome
Chiyoda-ku
Tokyo 100-0004
Japan

2) Japan Atomic Energy Agency
4-49, Muramatsu
Tokai-mura, Naka-gun
Ibaraki 319-1184
Japan

(74) **Agent :**
Patrick Mirandah
C/O Mirandah Asia (Malaysia) Sdn. Bhd.

(54) **Title :** Method for Synthesizing Rare Earth Metal Extractant

(57) **Abstract :**

A rare earth metal extractant containing, as the extractant component, dialkyldiglycol amide acid which is excellent in breaking down light rare earth elements is reacted in diglycolic acid (X mol) and an esterification agent (Y mol) at a reaction temperature of 70°C or more and for a reaction time of one hour or more such that the mol ratio of Y/X is 2.5 or more, and is subjected to vacuum concentration. Subsequently, a reaction intermediate product is obtained by removing unreacted products and reaction residue, and an aprotic polar solvent is added as the reaction solvent. Then, the reaction intermediate product is reacted with dialkyl amine (Z mol) such that the mol ratio of Z/X is 0.9 or more and the aprotic polar solvent is removed. As a consequence, a rare earth metal extractant is efficiently synthesized at a low cost and at a high yield without having to use expensive diglycolic acid anhydride and harmful dichloromethane.

DESCRIPTION

TITLE OF INVENTION

METHOD FOR SYNTHESIZING RARE EARTH METAL EXTRACTANT

TECHNICAL FIELD

[0001]

This invention relates to a method for synthesizing a rare earth metal extractant, especially suited for the extraction and separation of at least two of light rare earth elements (La, Ce, Pr, Nd, Sm, and Eu), or at least one of the light rare earth elements and at least one of other rare earth elements (inclusive of Y).

BACKGROUND ART

[0002]

In the modern society, rare earth elements are used in a wide variety of applications, for example, as rare earth magnets, phosphors, and electronic materials in nickel hydrogen batteries. With respect to the current supply of rare earth elements, a crisis of the rare earth resource is highlighted because the producers are limited, the price lacks stability, and the demand is expected to surpass the supply in the near future. For these reasons, many attempts are made to reduce the amount of rare earth element used and to develop a replacement. At the same time, it is desired to establish a recycle system for recovering rare earth elements as one valuable from in-process scraps produced during manufacture of products and municipal wastes like electric and electronic appliances collected from cities. Also there is an urgent need for the research and development of new rare earth mines.

[0003]

Known methods for separating rare earth elements include column extraction (or solid-liquid extraction) using ion exchange resins, and solvent extraction (or liquid-liquid extraction) using metal extractants. Although the column extraction (or solid-liquid extraction) method is simple in apparatus and easy in operation as compared with the solvent extraction method, it is small in extraction capacity and discourages rapid treatment. The column extraction method is thus used in the removal of a metal when the concentration of a metal to be extracted in a solution is low, that is, when the metal to be extracted is present as an impurity, as well as in the waste water treatment. On the other hand, the solvent extraction (or liquid-liquid extraction) method needs a complex apparatus and cumbersome operation as compared with the column extraction method, but provides for a large extraction capacity and rapid treatment. Thus the solvent extraction method is often used in industrial separation and purification of metal elements. For the separation and purification of rare earth elements that requires efficient treatment of a large volume through continuous steps, the solvent extraction method capable of such efficient treatment is often used.

[0004]

In the solvent extraction method, a water phase consisting of an aqueous solution containing metal elements to be separated is contacted with an organic phase consisting of an extractant for extracting a selected metal element and an organic solvent for diluting the extractant. Then the metal element is extracted with the extractant for separation.

[0005]

Known metal extractants used in the art include tributyl phosphate (TBP), carboxylic acids (e.g., Versatic Acid 10), phosphoric acid esters, phosphonic acid compounds, and phosphinic acid compounds. A typical phosphoric acid ester is di-2-ethylhexylphosphoric acid (D2EHPA), a typical phosphonic acid compound is 2-ethylhexylphosphoric acid-mono-2-ethylhexyl ester (PC-88A by Daihachi Chemical Industry Co., Ltd.), and a typical phosphinic acid compound is bis(2,4,4-trimethylpentyl)phosphoric acid (Cyanex 272 by

Cytec Industries). These extractants are commercially available and commonly used.

[0006]

The separation efficiency of the solvent extraction method depends on a separation ability of the metal extractant, specifically a separation factor thereof. As the separation factor is higher, the separation efficiency of the solvent extraction method is higher, which enables simplification of separating steps and scale-down of the separation apparatus, making the process efficient and eventually leading to a cost reduction. A low separation factor, on the other hand, makes the separation process complex and poses a need for a large-scale separation apparatus.

[0007]

Even PC-88A which is known to have a high separation factor for rare earth elements among the currently commercially available metal extractants has a low separation factor between elements of close atomic numbers, for example, a separation factor of less than 2, specifically about 1.4 between neodymium and praseodymium which are allegedly most difficult to separate among rare earth elements. The separation factor of this value is not sufficient for separation between neodymium and praseodymium. To separate them at an acceptable purity, a large-scale apparatus must be installed at the expense of cost. For more efficient separation of these elements, there is a desire for the development of a metal extractant having a higher separation factor than in the prior art and an extracting/separating method using the same.

[0008]

Dialkyl diglycol amic acids are known from Patent Document 1: JP-A 2007-327085 as the metal extractant having a high separation factor with respect to rare earth elements, specifically light rare earth elements such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), and samarium (Sm). Using this extractant in solvent extraction, the extraction/separation step of rare earth elements, specifically light rare earth elements can be made more efficient. In fact, better results are obtained from the extraction/separation step of light rare earth elements using dialkyl diglycol amic acid on a laboratory scale.

[0009]

When dialkyl diglycol amic acid was used as the metal extractant, satisfactory results were confirmed in a light rare earth element extraction/separation experiment which was conducted at a rare earth element concentration (C_A: 0.01 mol/L $\leq C_A \leq$ 0.7 mol/L) and a corresponding metal extractant concentration (C_0: 0.1 mol/L $\leq C_0 \leq$ 1.5 mol/L) which were practical operating conditions of the rare earth element separating process and in a light rare earth element extraction/separation experiment using a countercurrent multi-stage mixer/settler of a practically operating apparatus.

[0010]

The dialkyl diglycol amic acid exhibits a satisfactory separation factor in its performance as the metal extractant for separating light rare earth elements, as mentioned above, and its operating conditions have been surveyed. However, its synthesis has not been fully established.

[0011]

The known method for synthesizing the dialkyl diglycol amic acid follows the reaction scheme below.

[Chemical Formula 1]

$$C_4H_4O_4 \quad + \quad R^1R^2NH \xrightarrow[\text{in dichloromethane, 0 to 30°C}]{\text{in } CH_2Cl_2} R^1R^2NCOCH_2OCH_2COOH$$

diglycolic anhydride	secondary alkyl amine	in dichloromethane 0 to 30°C	dialkyl diglycol amic acid

Herein R^1 and R^2 are each independently alkyl, and at least one is a straight or branched alkyl group of at least 6 carbon atoms.

[0012]

First, diglycolic anhydride is suspended in dichloromethane. A secondary alkylamine in an amount slightly less than an equimolar amount to the diglycolic anhydride is dissolved in dichloromethane. The solution is mixed with the suspension at 0 to 30°C. As diglycolic anhydride reacts, the mixed solution becomes clear. The reaction is completed when the solution becomes clear. This is followed by removal of water-soluble impurities by washing with deionized water, removal of water with a dehydrating agent (e.g., sodium sulfate), filtration, and solvent removal. Recrystallization from hexane is repeated plural times for purification, yielding the desired product (Patent Document 1: JP-A 2007-327085).

[0013]

This synthesis method uses as the reaction solvent dichloromethane which is one of the harmful substances listed in the Chemical Substance Examination Law, Labor Safety and Health Regulations, Air Pollution Control Act, Water Pollution Control Act, Pollutant Release and Transfer Register (PRTR) and the like in Japan. It is recommended to avoid the substance. In addition, since the solubility of the reactant, diglycolic anhydride is not so high, the synthesis reaction becomes a solid-liquid reaction and has a poor reactivity.

[0014]

In fact, the above known synthesis method gives a yield of more than 90% because it is conducted only on a laboratory scale where the amount of synthesis is several grams. However, a prominent drop of yield occurs when the synthesis is enlarged to a scale of several kilograms or more. In fact, in a synthesis experiment conducted on a scale of several hundreds of grams, the yield decreases below 80%. Such a yield drop is unwanted.

[0015]

Further, since diglycolic anhydride is a relatively expensive chemical, the price of dialkyl diglycol amic acid synthesized therefrom is at least 3 times the price of commercially available metal extractants. This method has a significant effect of enhancing process efficiency due to excellent separation capability, but does not lead to a cost reduction of the overall process because of the increased expense of metal extractant.

Citation List

Patent Document

[0016]

Patent Document 1: JP-A 2007-327085

SUMMARY OF INVENTION

Technical Problem

[0017]

While the invention is made to overcome the outstanding problems, its object is to provide a method for synthesizing a rare earth metal extractant without a need for diglycolic anhydride as the reactant and dichloromethane as the reaction solvent in the prior art method while achieving advantages including improved yield of synthesized product, improved efficiency of synthesis process, and reduced cost of the desired metal extractant, dialkyl diglycol amic acid.

Solution to Problem

[0018]

The inventors made extensive investigations to solve the outstanding problems. With respect to the synthesis of a dialkyl diglycol amic acid serving as a rare earth metal extractant, the inventors have found that in the step of reacting a reaction intermediate product, which is obtained by reacting a reactant, diglycolic acid in an esterifying agent and then removing in vacuum the unreacted esterifying agent and the reaction residue, with a dialkylamine, if the ester formed is not isolated from the reaction intermediate product, an aprotic polar solvent is used as the reaction solvent, and the reaction solvent is removed at the end of reaction, then a rare earth metal extractant comprising a dialkyl diglycol amic acid as the active component can be synthesized. This method is successful in synthesizing a metal extractant in the form of dialkyl diglycol amic acid in high yields, at high efficiency and at low cost. The invention is predicated on this finding.

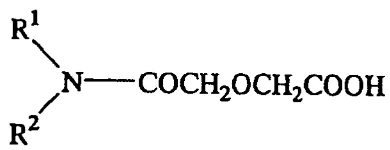
[0019]

Accordingly, the invention provides a method for synthesizing a rare earth metal extractant as defined below.

Claim 1:

A method for synthesizing a rare earth metal extractant comprising a dialkyl diglycol amic acid having the general formula (1):

[Chemical Formula 2]



(1)

wherein R^1 and R^2 are each independently an alkyl group, at least one of R^1 and R^2 is a straight or branched alkyl group having at least 6 carbon atoms, as the active component, said method comprising the steps of:

reacting X mole of diglycolic acid with Y mole of an esterifying agent, with a molar ratio of Y/X being at least 2.5, at a reaction temperature of at least 70°C for a reaction time of at least 1 hour, then concentrating in vacuum to remove unreacted reactant and reaction residue, thus obtaining a reaction intermediate product,

adding a reaction solvent to the reaction intermediate product, the reaction solvent being an aprotic polar solvent,

reacting the reaction intermediate product with Z mole of a dialkylamine, with a molar ratio of Z/X being at least 0.9, and

removing the aprotic polar solvent.

Claim 2:

A method for synthesizing a rare earth metal extractant according to claim 1 wherein the esterifying agent is selected from acetic anhydride and trifluoroacetic anhydride.

Claim 3:

A method for synthesizing a rare earth metal extractant according to claim 1 or 2 wherein the aprotic polar solvent is selected from the group consisting of acetone, acetonitrile, tetrahydrofuran, N,N-dimethylformamide, and dimethyl sulfoxide.

Claim 4:

A method for synthesizing a rare earth metal extractant according to any one of claims 1 to 3 wherein in the step of reacting diglycolic acid with an esterifying agent, the molar ratio of Y/X is in the range: $2.5 \le Y/X \le 6.5$.

Claim 5:

A method for synthesizing a rare earth metal extractant according to any one of claims 1 to 4 wherein in the step of reacting the reaction intermediate product between diglycolic acid and esterifying agent with a dialkylamine, the molar ratio of Z/X is in the range: $0.9 \le Z/X \le 1.2$.

Advantageous Effects of Invention

[0020]

According to the rare earth metal extractant synthesis method of the invention, a dialkyl diglycol amic acid, which is effective for the separation of light rare earth elements, can be synthesized at high efficiency and low cost and in high yields without a need for expensive diglycolic anhydride and harmful dichloromethane. The method is of great worth in the industry.

BRIEF DESCRIPTION OF DRAWINGS

[0021]

FIG. 1 is a ^{1}H-NMR (in solvent $CDCl_3$) chart of the reaction product D2EHDGAA synthesized in Example 1.

FIG. 2 is a ^{1}H-NMR (in solvent $CDCl_3$) chart of the reaction product DODGAA synthesized in Example 2.

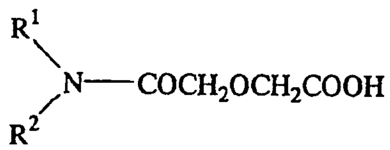
DESCRIPTION OF EMBODIMENTS

[0022]

Now the invention is described in detail.

The invention pertains to a rare earth metal extractant which comprises a dialkyl diglycol amic acid having the general formula (1) as the active component.

[Chemical Formula 3]



(1)

[0023]

Herein R^1 and R^2 are each independently alkyl, and at least one of R^1 and R^2 is a straight or branched alkyl group of at least 6 carbon atoms, preferably 6 to 18 carbon atoms, and more preferably 7 to 12 carbon atoms. If the carbon count is less than 6, the compound fails to play the role of extractant because it is less lipophilic so that the organic phase lacks stability and exhibits poor separation from the aqueous phase, and because the dissolution of the extractant itself in aqueous phase becomes noticeable. An excessive carbon count contributes to no improvements in basic abilities like extraction and separation abilities despite the increased cost of extractant manufacture. As long as lipophilic nature is ensured, if one of R^1 and R^2 has a carbon count of at least 6, then the other may be of less than 6 carbon atoms. Preferred examples include a compound of formula (1) wherein two octyl ($-C_8H_{17}$) groups are introduced, which is named N,N-dioctyl-3-oxapentane-1,5-amic acid or dioctyl diglycol amic acid (abbreviated as DODGAA, hereinafter); and a compound of formula (1) wherein two 2-ethylhexyl ($-CH_2CH(C_2H_5)C_4H_9$) groups are introduced, which is named N,N-bis(2-ethylhexyl)-3-oxapentane-1,5-amic acid or di(2-ethylhexyl) diglycol amic acid (abbreviated as D2EHDGAA, hereinafter).

[0024]

According to the invention, the rare earth metal extractant which comprises a dialkyl diglycol amic acid is synthesized by reacting diglycolic acid as one reactant with an esterifying agent, then concentrating in vacuum to remove a low-boiling fraction including unreacted esterifying agent and reaction residue (the esterifying agent hydrolyzate resulting from reaction of the esterifying agent with diglycolic acid), thus obtaining a reaction intermediate product, reacting the reaction intermediate product with a dialkylamine in an aprotic polar solvent, and removing the aprotic polar solvent at the end of reaction. For example, diglycolic acid is first dissolved in the esterifying agent and aged therein. The reaction intermediate product is collected by vacuum concentration. The reaction intermediate product is dissolved in an aprotic polar solvent. Then the dialkylamine is added to the solution, which is mixed for reaction. The dialkylamine used herein is a secondary alkylamine having alkyl groups corresponding to R^1 and R^2 in formula (1) representative of the dialkyl diglycol amic acid.

[0025]

In the synthesis method of the invention, diglycolic acid is reacted in the esterifying agent at a temperature of at least 70°C for a time of at least 1 hour.

[0026]

A reaction temperature below 70°C provides a low reaction rate, making it difficult to achieve a conversion in excess of 90% or taking an extremely long time for sufficient reaction. Therefore, the reaction temperature is at least 70°C, preferably 70 to 140°C, and more preferably 80 to 120°C.

[0027]

Also, if the reaction time is less than 1 hour, the reaction may not reach a sufficient conversion, failing to form a reaction product having a purity and yield of at least 90% both. Therefore, the reaction time is at least 1 hour, preferably 1 to 6 hours, and more preferably 2 to 4 hours.

[0028]

This reaction does not quickly proceed if a molar ratio Y/X is less than 2.5 wherein the amount of diglycolic acid is X mole and the amount of the esterifying agent is Y mole. Then the reaction intermediate product and eventually the desired extractant, dialkyl diglycol amic acid are insufficient in yield and purity. The range of Y/X that ensures an acceptable yield and a purity of at least 90% is a molar ratio Y/X of at least 2.5, preferably $2.5 \leq Y/X \leq 6.5$, and more preferably $3.5 \leq Y/X \leq 5.5$.

[0029]

While the intermediate product resulting from the above reaction is composed mostly of diglycolic anhydride, it contains minor amounts of unreacted diglycolic acid, esterifying agent and impurities contained in the reactant, diglycolic acid. Once the reaction of diglycolic acid with the esterifying agent is conducted by the synthesis method of the invention, the metal extractant comprising dialkyl diglycol amic acid synthesized can be obtained at a practically acceptable purity. To improve the purity of dialkyl diglycol amic acid as the metal extractant, water-soluble impurities may be removed by water washing. However, such purification is unnecessary on practical use because impurities have no impact on the capability to extract and separate rare earth metals.

[0030]

The esterifying agent used herein is selected from low-boiling compounds because the reaction with the esterifying agent is followed by vacuum concentration (vacuum drying) to remove (or distill off) the unreacted reactant and reaction residue while diglycolic anhydride is left. The esterifying agent is an agent capable of dehydration and condensation of two carboxyl groups on diglycolic acid and includes, for example, acetic anhydride and trifluoroacetic anhydride. Since the synthesis method of the invention uses the esterifying agent which can be distilled off in vacuum, the method eliminates a need for the step of water washing for improving the purity of dialkyl diglycol amic acid, that is, water washing away the esterifying agent.

[0031]

The reaction solvent used herein is an aprotic polar solvent. It refers to a solvent which is amphiphatic, i.e., both hydrophilic and lipophilic. Examples of the aprotic polar solvent include acetone, acetonitrile, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Of these, acetone and tetrahydrofuran (THF) are preferred from the standpoints of solvent removal in the synthesis process and legal inhibitions on solvents as by the PRTR or the like. When an aprotic polar solvent is used as the reaction solvent, the reaction intermediate product between diglycolic acid and esterifying agent and the dialkylamine are readily dissolved in the reaction solvent. Thus the synthesis reaction becomes a liquid-liquid reaction featuring a high reactivity.

[0032]

When a nonpolar solvent is used as the reaction solvent, the dialkylamine which is lipophilic is readily dissolved in the reaction solvent, but the reaction intermediate product between diglycolic acid and esterifying agent which is hydrophilic has a low solubility in the reaction solvent. Thus the synthesis reaction becomes a solid-liquid reaction, leading to a poor reactivity. On the other hand, when a protic polar solvent is used as the reaction solvent, the solubilities of the reaction intermediate product and the dialkylamine in the solvent differ depending on the type of solvent. For example, when the reaction solvent is water, the reaction intermediate product is readily dissolved therein, but its reactivity with dialkylamine substantially drops because diglycolic anhydride in the reaction intermediate product ceases to be anhydride, and thus little reaction takes place.

[0033]

Also, when the reaction solvent is an alcohol, the dialkylamine is readily dissolved in the reaction solvent, but diglycolic anhydride in the reaction intermediate product has a low solubility in the reaction solvent. Thus the synthesis reaction becomes a solid-liquid reaction, leading to a poor reactivity. Additionally, part of diglycolic anhydride forms an alkyl ester with the alcohol. As a result, the alkyl ester of diglycolic acid is left as impurity, and the amount of dialkyl diglycol amic acid formed by the reaction is reduced. Furthermore, the reaction produces not only the desired dialkyl diglycol amic acid, but also an alkyl ester of dialkyl diglycol amic acid as by-product. The alkyl ester of diglycolic acid and the alkyl ester of dialkyl diglycol amic acid form a complex with a rare earth metal ion, have some extraction capability as the rare earth metal extractant, but substantially no separation capability, and thus become an inhibitory factor to the extraction/separation behavior during solvent extraction. In conclusion, when the alcohol is used as the reaction solvent, the resulting reaction product is extremely inferior in the separation of rare earth elements as the rare earth metal extractant.

[0034]

Furthermore, in the prior art synthesis method, the desired product is recovered at the end of reaction through steps of removal of water-soluble impurities by deionized water washing, removal of water with a dehydrating agent, filtration, solvent removal, and further conducting recrystallization and decantation using hexane plural times for purification. Although it is acceptable to carry out post-treatments after the completion of reaction including removal of water-soluble impurities by deionized water washing, removal of water with a dehydrating agent, filtration, recrystallization and decantation of the reaction solution, the synthesis method of the invention eliminates a need for such post-treatments after the completion of reaction and allows the desired metal extractant to be recovered merely by removing the solvent. The synthesis method of the invention is a liquid-liquid reaction rather than a solid-liquid reaction as in the prior art method, and thus ensures so high a reactivity as to minimize the unreacted reactant, substantially eliminating a need for post-treatment to remove impurities.

[0035]

In the metal extractant synthesis method of the invention, the ratio (Z/X) of the amount (Z mole) of dialkylamine to the amount (X mole) of diglycolic acid is at least 0.9, preferably 0.9 ≤ Z/X ≤ 1.2, and more preferably 0.95 ≤ Z/X ≤ 1.1, when the purity of diglycolic anhydride contained as the major component in the intermediate product obtained from reaction of diglycolic acid with esterifying agent and vacuum concentration is taken into account. The reaction product obtained from the inventive method contains unreacted dialkylamine as well as the desired dialkyl diglycol amic acid. In the prior art method, purification steps such as recrystallization and decantation are performed plural times in order to remove the unreacted dialkylamine. With the inventive method, the metal extractant with residual dialkylamine may be used in solvent extraction because its separation and phase separation capabilities are not impaired at all and satisfactory extraction and separation is possible. That is, since the dialkylamine remaining in the metal extractant or the organic phase for solvent extraction does not become an inhibitory factor to extraction and separation, it is unnecessary to remove the dialkylamine as the impurity. The synthesis process is thus simplified. In addition, since any loss of the reaction product during purification such as recrystallization and decantation is minimized, the yield is improved.

[0036]

In case Z/X > 1.2, the reaction product may contain an excess of unreacted dialkylamine as well as the desired dialkyl diglycol amic acid. In this case, the reaction product can be used as the extractant because its separation and phase separation capabilities during solvent extraction are not impaired, but the use of an excess of dialkylamine is meaningless. This setting is not advantageous in that the cost of reactant for synthesis is increased.

[0037]

In case Z/X < 0.9, although the desired dialkyl diglycol amic acid is obtained as the reaction product, an excessive amount of diglycolic anhydride resulting from diglycolic acid is reacted. As a result, a noticeable amount of unreacted diglycolic acid is left in the reaction product. When solvent extraction is carried out using the metal extractant with residual diglycolic acid, not only a satisfactory separation capability is lost, but also a crud develops at the interface between organic and aqueous phases to turn white turbid, resulting in poor phase separation and inhibiting normal extraction and separation. This indicates that the diglycolic acid remaining along with the metal extractant forms a complex with a rare earth metal ion, thus inhibiting satisfactory separation and extraction. It is believed that diglycolic acid becomes an inhibitory factor to separation and extraction. To obtain diglycolic acid-free dialkyl diglycol amic acid as the rare earth metal extractant capable of normal extraction and separation, the step of removing unreacted diglycolic acid, that is, the step of removing the reaction solvent and washing the reaction product with water to remove water-soluble diglycolic acid is necessary as in the prior art method. However, on water washing, the dialkyl diglycol amic acid having a very low solubility in water may crystallize and precipitate in the solvent (for example, DODGAA has a solubility in water of 6.2×10^{-6} mol/L). To use the crystallized dialkyl diglycol amic acid as the rare earth metal extractant, it must be filtered and dried. Thus extra steps are necessary as compared with the embodiment wherein the ratio Z/X is $0.9 \leq Z/X \leq 1.2$, and the process is less efficient.

EXAMPLES

[0038]

Examples and Comparative Examples are given below by way of illustration and not by way of limitation.

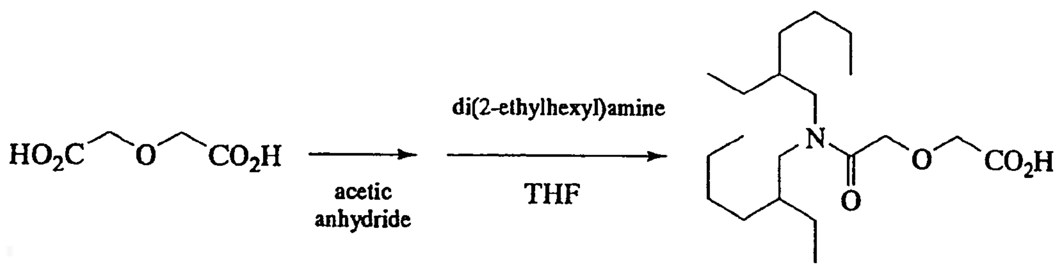
[0039]

Example 1 and Comparative Example 1

A mixed solution of 27 g (0.20 mole) of diglycolic acid and 130 g (1.27 moles) of acetic anhydride was heated under reflux for 4 hours. Thereafter, the excess acetic anhydride and acetic acid formed by reaction were distilled off in vacuum. To the concentrate (reaction intermediate), 150 g of tetrahydrofuran was added, and then 48 g (0.20 mole) of di(2-ethylhexyl)amine was added dropwise. Stirring was continued for 2 hours at room temperature, followed by vacuum concentration to remove the reaction solvent, tetrahydrofuran, yielding 70 g of the reaction product as a pale yellow liquid (Example 1). The reaction scheme is as shown below.

[0040]

[Chemical Formula 4]



[0041]

A portion of the reaction product was taken out and analyzed by ^{1}H-NMR spectroscopy. The reaction product was identified to be the desired D2EHDGAA (FIG. 1). The yield of D2EHDGAA was 98%.

[0042]

In another run, 150 g of tetrahydrofuran was added to 27 g (0.20 mole) of diglycolic acid, and then 48 g (0.20 mole) of di(2-ethylhexyl)amine was added dropwise. Stirring was continued for 2 hours at room temperature, followed by vacuum concentration to remove the reaction solvent, tetrahydrofuran, yielding the reaction product as a pale yellow liquid (Comparative Example 1).

[0043]

Next, an extraction/separation performance test was carried out. The stoichiometric amount of the reaction product, D2EHDGAA in Example 1 or Comparative Example 1 was diluted with hexanol to form an organic solution having a D2EHDGAA concentration of 0.3 mol/L, which might become an organic phase.

[0044]

A mixed rare earth metal aqueous solution was prepared by dissolving praseodymium chloride and neodymium chloride in water in a molar ratio Pr:Nd of 1:1 and a concentration of 0.1 mol/L of Pr+Nd to form an aqueous solution, which might become an aqueous phase. A separatory funnel was charged with 100 mL of the organic solution and 100 mL of the aqueous solution and shaken at 20°C for about 20 minutes to effect extraction. After equilibrium was reached, the liquid was allowed to separate into organic and aqueous phases. A separatory funnel was charged with 100 mL of the thus separated organic phase and 100 mL of 5N hydrochloric acid and shaken at 20°C for about 20 minutes whereby the rare earth element once extracted in the organic phase was back extracted in the hydrochloric acid aqueous solution. The concentrations of praseodymium and neodymium in the aqueous phase and the back-extracted hydrochloric acid aqueous solution were measured by an ICP atomic emission spectrometer ICP-7500 (Shimadzu Corp.). The Nd/Pr separation factor and phase separation are reported in Table 1.

[0045]

Table 1

	Esterifying agent	Nd/Pr separation factor	Phase separation
Example 1	acetic anhydride	2.5	definite
Comparative Example 1	nil	-	indefinite

[0046]

For the reaction product obtained in Example 1, its Nd/Pr separation factor indicative of the separation ability as a metal extractant was satisfactory, and the phase separation state was definite. For the reaction product obtained in Comparative Example 1, the phase separation state was indefinite and its Nd/Pr separation factor was unmeasurable.

[0047]

Example 2 and Comparative Example 2

A mixed solution of 40 g (0.3 mole) of diglycolic acid and 180 g (1.76 moles) of acetic anhydride was heated under reflux for 4 hours. Thereafter, the excess acetic anhydride and acetic acid formed by reaction were distilled off in vacuum. To the concentrate (reaction intermediate), 200 g of acetone was added, and then 72.5 g (0.3 mole) of dioctylamine was added dropwise. Stirring was continued for 2 hours at room temperature, followed by vacuum concentration to remove the reaction solvent, acetone, yielding the reaction product as a white solid (Example 2).

[0048]

A portion of the reaction product was taken out and analyzed by ^{1}H-NMR spectroscopy. The reaction product was identified to be the desired DODGAA (FIG. 2). The yield of DODGAA was 98%.

[0049]

By the same procedure as above aside from using hexanol as the reaction solvent, the reaction product was obtained as a white solid (Comparative Example 2).

[0050]

Next, an extraction/separation performance test was carried out. The stoichiometric amount of the reaction product, DODGAA in Example 2 or Comparative Example 2 was diluted with hexanol to form an organic solution having a DODGAA concentration of 0.3 mol/L, which might become an organic phase.

[0051]

A mixed rare earth metal aqueous solution was prepared by dissolving praseodymium chloride and neodymium chloride in water in a molar ratio Pr:Nd of 1:1 and a concentration of 0.1 mol/L of Pr+Nd to form an aqueous solution, which might become an aqueous phase. A separatory funnel was charged with 100 mL of the organic solution and 100 mL of the aqueous solution and shaken at 20°C for about 20 minutes to effect extraction. After equilibrium was reached, the liquid was allowed to separate into organic and aqueous phases. A separatory funnel was charged with 100 mL of the thus separated organic phase and 100 mL of 5N hydrochloric acid and shaken at 20°C for about 20 minutes whereby the rare earth element once extracted in the organic phase was back extracted in the hydrochloric acid aqueous solution. The concentrations of praseodymium and neodymium in the aqueous phase and the back-extracted hydrochloric acid aqueous solution were measured by an ICP atomic emission spectrometer ICP-7500 (Shimadzu Corp.). The Nd/Pr separation factor and phase separation are reported in Table 2.

[0052]

Table 2

	Reaction solvent	Nd/Pr separation factor	Phase separation
Example 2	acetone	2.5	definite
Comparative Example 2	hexanol	1.3	indefinite

[0053]

For the reaction product obtained in Example 2, its Nd/Pr separation factor indicative of the separation ability as a metal extractant was satisfactory, and the phase separation state was definite. For the reaction product obtained in Comparative Example 2, its Nd/Pr separation factor and the phase separation state were inferior to Example 2. The indefinite phase separation state indicates that the product is inadequate for solvent extraction.

[0054]

Examples 3, 4 and Comparative Examples 3, 4

A mixed solution of 13.4 g (0.1 mole) of diglycolic acid and 60 g (0.59 mole) of acetic anhydride was heated under reflux under the conditions shown in Table 3. Thereafter, the excess acetic anhydride and acetic acid formed by reaction were distilled off in vacuum. To the concentrate (reaction intermediate), 200 g of acetone was added, and then 24.1 g (0.1 mole) of di(2-ethylhexyl)amine was added dropwise. Stirring was continued for 2 hours at room temperature, followed by vacuum concentration to remove the reaction solvent, acetone, yielding the reaction product as a pale yellow liquid.

[0055]

Next, an extraction/separation performance test was carried out. The stoichiometric amount of the reaction product, D2EHDGAA in Example 3, 4 or Comparative Example 3, 4 was diluted with kerosene to form an organic solution having a D2EHDGAA concentration of 0.3 mol/L, which might become an organic phase.

[0056]

A mixed rare earth metal aqueous solution was prepared by dissolving praseodymium chloride and neodymium chloride in water in a molar ratio Pr:Nd of 1:1 and a concentration of 0.1 mol/L of Pr+Nd to form an aqueous solution, which might become an aqueous phase. A separatory funnel was charged with 100 mL of the organic solution and 100 mL of the aqueous solution and shaken at 20°C for about 20 minutes to effect extraction. After equilibrium was reached, the liquid was allowed to separate into organic and aqueous phases. A separatory funnel was charged with 100 mL of the thus separated organic phase and 100 mL of 5N hydrochloric acid and shaken at 20°C for about 20 minutes whereby the rare earth element once extracted in the organic phase was back extracted in the hydrochloric acid aqueous solution. The concentrations of praseodymium and neodymium in the aqueous phase and the back-extracted hydrochloric acid aqueous solution were measured by an ICP atomic emission spectrometer ICP-7500 (Shimadzu Corp.). The Nd/Pr separation factor and phase separation are reported in Table 3.

[0057]

Table 3

	Reaction temperature (°C)	Reaction time (hr)	Nd/Pr separation factor	Phase separation
Example 3	70	4	2.5	definite
Example 4	120	2	2.5	definite
Comparative Example 3	30	2	1.4	indefinite
Comparative Example 4	140	0.5	1.8	indefinite

[0058]

In Examples 3 and 4 wherein the conditions of reaction between diglycolic acid and acetic anhydride include a temperature of at least 70°C and a time of at least 1 hour, their Nd/Pr separation factor indicative of the separation ability as a metal extractant and the phase separation state were satisfactory. In Comparative Examples 3 and 4 wherein the reaction conditions are outside the ranges, their Nd/Pr separation factor and the phase separation state were inferior.

[0059]

Examples 5, 6 and Comparative Examples 5, 6

A mixed solution of an amount (X mole) of diglycolic acid, shown in Table 4, and an amount (Y mole) of acetic anhydride, shown in Table 4, was heated under reflux for 4 hours. Thereafter, the excess acetic anhydride and acetic acid formed by reaction were distilled off in vacuum. To the concentrate (reaction intermediate), 400 g of THF was added, and then an amount (Z mole) of di(2-ethylhexyl)amine, shown in Table 4, was added dropwise. Stirring was continued for 2 hours at room temperature, followed by vacuum concentration to remove the reaction solvent, THF, yielding the reaction product as a pale yellow liquid. Table 4 also reports the ratio Y/X which is the amount (Y mole) of acetic anhydride as the esterifying agent divided by the amount (X mole) of diglycolic acid and the ratio

Z/X which is the amount (Z mole) of di(2-ethylhexyl)amine divided by the amount (X mole) of diglycolic acid.

[0060]

Next, an extraction/separation performance test was carried out. The stoichiometric amount of the reaction product, D2EHDGAA in Example 5, 6 or Comparative Example 5, 6 was diluted with toluene to form an organic solution having a D2EHDGAA concentration of 0.3 mol/L, which might become an organic phase.

[0061]

A mixed rare earth metal aqueous solution was prepared by dissolving praseodymium chloride and neodymium chloride in water in a molar ratio Pr:Nd of 1:1 and a concentration of 0.1 mol/L of Pr+Nd to form an aqueous solution, which might become an aqueous phase. A separatory funnel was charged with 100 mL of the organic solution and 100 mL of the aqueous solution and shaken at 20°C for about 20 minutes to effect extraction. After equilibrium was reached, the liquid was allowed to separate into organic and aqueous phases. A separatory funnel was charged with 100 mL of the thus separated organic phase and 100 mL of 5N hydrochloric acid and shaken at 20°C for about 20 minutes whereby the rare earth element once extracted in the organic phase was back extracted in the hydrochloric acid aqueous solution. The concentrations of praseodymium and neodymium in the aqueous phase and the back-extracted hydrochloric acid aqueous solution were measured by an ICP atomic emission spectrometer ICP-7500 (Shimadzu Corp.). The Nd/Pr separation factor and phase separation are reported in Table 4.

[0062]

Table 4

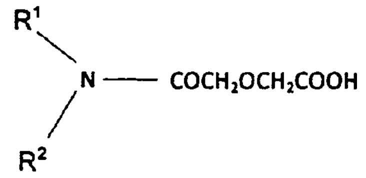
	X		Y		Z		Y/X	Z/X	Nd/Pr separation factor	Phase separation
	diglycolic acid		acetic anhydride		di(2-ethyl-hexyl)amine					
	g	mol	g	mol	g	mol				
Example 5	67.0	0.50	127.6	1.25	108.7	0.45	2.5	0.9	2.5	definite
Example 6	67.0	0.50	331.8	3.25	144.9	0.60	6.5	1.2	2.5	definite
Comparative Example 5	67.0	0.50	76.6	0.75	144.9	0.60	1.5	1.2	1.8	indefinite
Comparative Example 6	67.0	0.50	127.6	1.25	96.6	0.40	2.5	0.8	2.0	indefinite

[0063]

In Examples 5 and 6 wherein the amounts of diglycolic acid (X mole), acetic anhydride (Y mole) and di(2-ethylhexyl)amine (Z mole) are such that molar ratio Y/X is at least 2.5 and Z/X is at least 0.9, their Nd/Pr separation factor indicative of the separation ability as a metal extractant and the phase separation state were satisfactory. In Comparative Example 5 wherein Y/X < 2.5 and Comparative Example 6 wherein Z/X < 0.9, the phase separation state was indefinite because the excess diglycolic acid became an inhibitory factor to extraction, and their Nd/Pr separation factor was lower than in Examples.

CLAIMS :

1. A method for synthesizing a rare earth metal extractant comprising a dialkyl diglycol amic acid having the general formula (1):



(1)

wherein R^1 and R^2 are each independently an alkyl group, at least one of R^1 and R^2 is a straight or branched alkyl group having at least 6 carbon atoms, as the active component, said method comprising the steps of:

reacting X mole of diglycolic acid with Y mole of an esterifying agent, with a molar ratio of Y/X being at least 2.5, at a reaction temperature of at least 70° C for a reaction time of at least 1 hour, then concentrating in vacuum to remove unreacted reactant and reaction residue, thus obtaining a reaction intermediate product, the reaction intermediate product being obtained by concentrating so that the reaction intermediate product contains diglycolic anhydride having a purity of at least 90%, and further contains minor amounts of unreacted diglycolic acid and unreacted esterifying agent, and without further purification,

adding a reaction solvent to the reaction intermediate product, the reaction solvent being an aprotic polar solvent,

reacting the reaction intermediate product with Z mole of a dialkylamine, with a molar ratio of Z/X being at least 0.9, and

removing the aprotic polar solvent.

2. The method for synthesizing a rare earth metal extractant according to claim 1 wherein the esterifying agent is selected from acetic anhydride and trifluoroacetic anhydride.

3. The method for synthesizing a rare earth metal extractant according to claim 1 wherein the aprotic polar solvent is selected from the group consisting of acetone, acetonitrile, tetrahydrofuran, N,N-dimethylformamide, and dimethyl sulfoxide.

4. The method for synthesizing a rare earth metal extractant according to claim 1 wherein in the step of reacting diglycolic acid with an esterifying agent, the molar ratio of Y/X is in the range: 2.5≦Y/X≦6.5.

5. The method for synthesizing a rare earth metal extractant according to claim 1 wherein in the step of reacting the reaction intermediate product between diglycolic acid and esterifying agent with a dialkylamine, the molar ratio of Z/X is in the range: $0.9 \leqq Z/X \leqq 1.2$.

6. The method of synthesizing a rare earth metal extractant according to claim 1 wherein both R^1 and R^2 are each independently an alkyl group of 6 to 18 carbon atoms.

7. The method for synthesizing a rare earth metal extractant according to claim 1 wherein the aprotic polar solvent is selected from the group consisting of acetone, acetonitrile, N,N-dimethylformamide, and dimethyl sulfoxide.

8. The method for synthesizing a rare earth metal extractant according to claim 1 wherein the aprotic polar solvent comprises acetone.

9. The method for synthesizing a rare earth metal extractant according to claim 5 wherein the molar ratio of Z/X is in the range: $0.95 \leqq Z/X \leqq 1.1$.

10. The method for synthesizing a rare earth metal extractant according to claim 1 wherein the reaction intermediate product is directly used in the adding step.

11. The method for synthesizing a rare earth metal extractant according to claim 1 wherein the reaction intermediate product is not refined.

ABSTRACT

METHOD FOR SYNTHESIZING RARE EARTH METAL EXTRACTANT

A rare earth metal extractant containing, as the extractant component, dialkyldiglycol amide acid which is excellent in breaking down light rare earth elements is reacted in diglycolic acid (X mol) and an esterification agent (Y mol) at a reaction temperature of 70° C or more and for a reaction time of one hour or more such that the mol ratio of Y/X is 2.5 or more, and is subjected to vacuum concentration. Subsequently, a reaction intermediate product is obtained by removing unreacted products and reaction residue, and an aprotic polar solvent is added as the reaction solvent. Then, the reaction intermediate product is reacted with dialkyl amine (Z mol) such that the mol ratio of Z/X is 0.9 or more and the aprotic polar solvent is removed. As a consequence, a rare earth metal extractant is efficiently synthesized at a low cost and at a high yield without having to use expensive diglycolic acid anhydride and harmful dichloromethane.

FIG.1

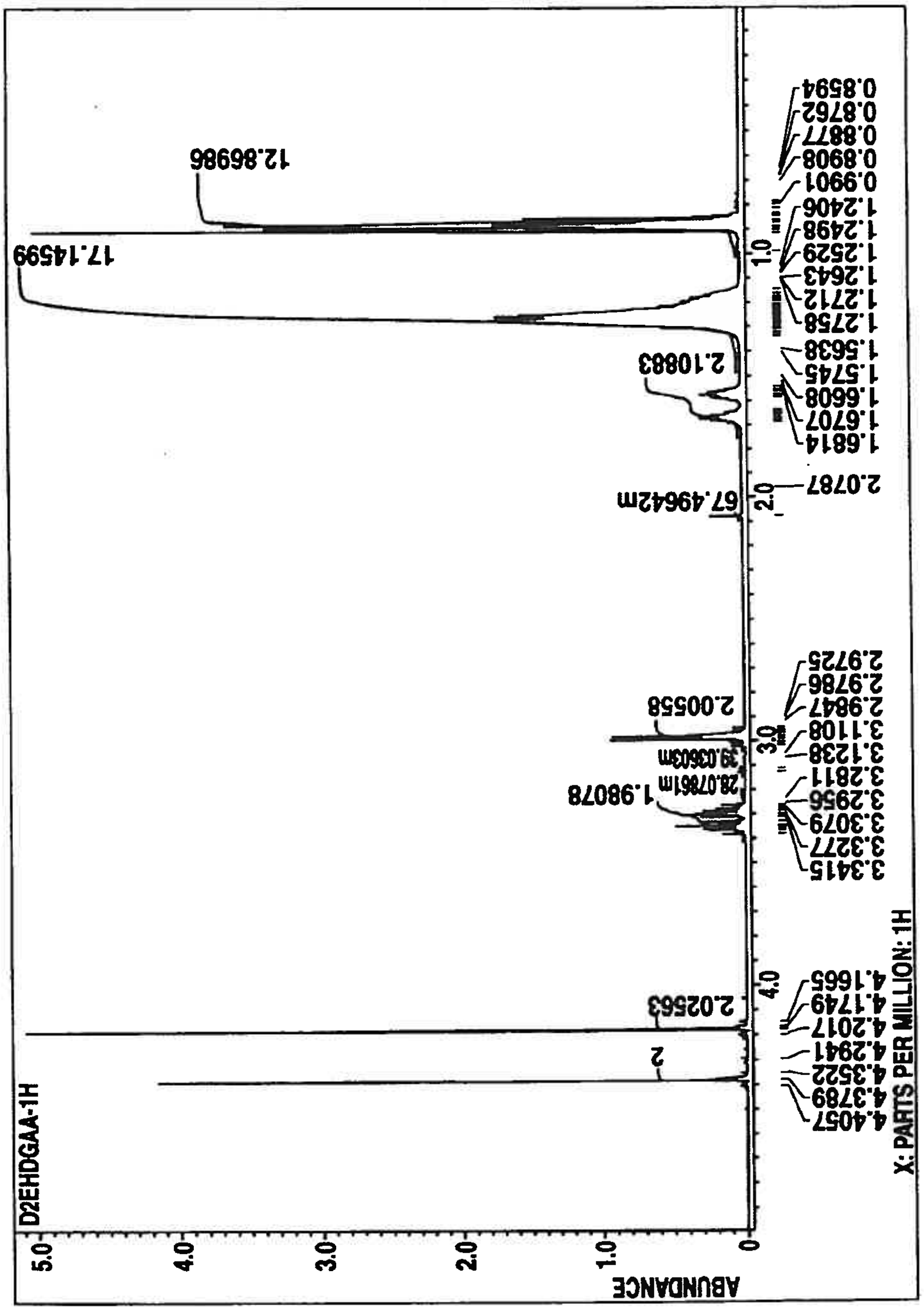
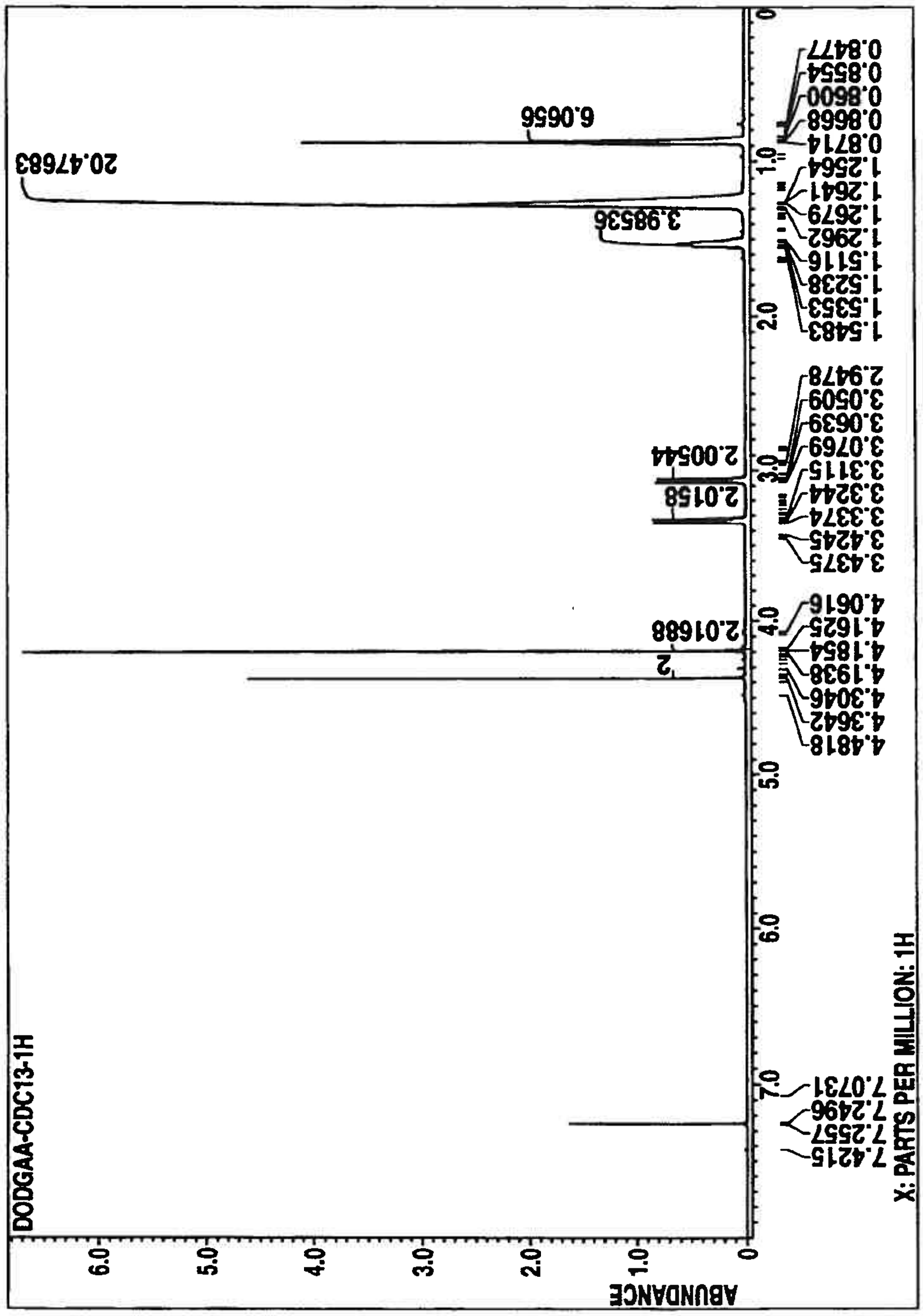

D2EHDGAA-1H
ABUNDANCE
X: PARTS PER MILLION: 1H
12.86986
17.14599
2.10883
67.4964 2m
2.00558
39.03603m
28.07861m
1.98078
2.02563
2
0.8594
0.8762
0.8877
0.8908
0.9901
1.2406
1.2498
1.2529
1.2643
1.2712
1.2758
1.5638
1.5745
1.6608
1.6707
1.6814
2.0787
2.9725
2.9786
2.9847
3.1108
3.1238
3.2811
3.2956
3.3079
3.3277
3.3415
4.1665
4.1749
4.2017
4.2941
4.3522
4.3789
4.4057

FIG.2


DODGAA-CDC13-1H
ABUNDANCE
X: PARTS PER MILLION: 1H
20.47683
6.0656
3.98536
2.00544
2.0158
2.01688
2
0.8477
0.8554
0.8600
0.8668
0.8714
1.2564
1.2641
1.2679
1.2962
1.5116
1.5238
1.5353
1.5483
2.9478
3.0509
3.0639
3.0769
3.3115
3.3244
3.3374
3.4245
3.4375
4.0616
4.1625
4.1854
4.1938
4.3046
4.3642
4.4818
7.0731
7.2496
7.2557
7.4215