

# Solvent Extraction of $\text{La}^{3+}$ with Ethylenediamine-N,N'-ditetradecyl-N,N'-diacetic Acid(EDDAT) in Dichloromethane

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Ethylenediamine-N,N'-ditetradecyl-N,N'-diacetic acid (EDDAT) was synthesized for the solvent extraction of  $\text{La}^{3+}$ . EDDAT was prepared from ethylenediamine-N,N'-diacetic acid (EDDA) and tetradecyl bromide in a basic n-amylalcohol-ethanol-water solvent system. The structure of this new extracting reagent was identified according to spectroscopic data, i.e.  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR, and elemental analysis results. The solvent extraction of  $\text{La}^{3+}$  with EDDAT in dichloromethane was studied as a function of parameters of the aqueous and organic phases. The optimal extraction conditions were determined. The extraction yield increased with a decrease in hydrogen ions in the aqueous phase. Stripping of the  $\text{La}^{3+}$  loaded organic phase was achieved with HCl aqueous solution. The effect of stripping as a function of the HCl concentration was also studied.

## Introduction

Solvent extraction is an effective separation method and is widely used in basic analytical chemistry, such as in the separation and concentration of metal ions, and in industry. A systematic study of the chelating extraction behavior of a series of representative trivalent lanthanoid ions was carried out with various chelating extractants, such as 8-quinolinol and its derivatives<sup>1-4</sup>, acylpyrazolones<sup>5-6</sup>,  $\beta$ -diketones<sup>7-9</sup> and N-benzoyl-N-phenyl-hydroxylamine (BPHA) and its derivatives<sup>10</sup>, both alone and in combination with adductants. BPHA and its analogues are extensively used as organic precipitant reagents for the spectrophotometric determination of several metal ions and solvent extractant. This is because they react with several metal ions to form stable chelates that are soluble in organic solvents<sup>11</sup>. Furthermore, hydrophobic chelating reagents having long alkyl chains have become of interest in recent years owing to their extraction behavior with metal ions<sup>12</sup>.

Work has recently been done on chelating reagents having long-chain alkyl groups because of their successful use in hydrometallurgical separation<sup>13</sup>. They have high solubility in nonpolar solvents and low solubility in water. The former is related to the loading capacity of the chelating reagents; the latter prevents their loss during multicyclic extractions. The aim of the present study was to identify a new extracting reagent with a different functional group for the extraction of  $\text{La}^{3+}$ . For this purpose the long-

chain alkyl group ethylenediamine-N,N'-ditetradecyl-N,N'-diacetic acid (EDDAT) was used. This can easily be synthesized and is a very useful organic reagent for the extraction of  $\text{La}^{3+}$  ion due to its extractability.

## Experimental

### Reagent and Apparatus

Infrared spectra were recorded on a Midac 1700 FTIR instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a Bruker-Avance DPX 400 spectrometer in  $\text{CDCl}_3$  solvent containing 1 %  $\text{Me}_4\text{Si}$  and were recorded in ppm( $\delta$ ) downfield from internal  $\text{Me}_4\text{Si}$ . Elemental analyses were performed on a Carlo-Erba Model 1200 instrument. The equilibrium pH was measured using a RCN AL-ON, MP 8100 precision model pH meter. A Heidolph Type RZR 50 model mechanical stirrer and Grand Type W14 model water circulator thermostatic baths were used in the solvent extraction experiments.  $\text{La}^{3+}$  concentrations in the aqueous phase were determined with a Shimadzu 160 model UV-Visible spectrophotometer.

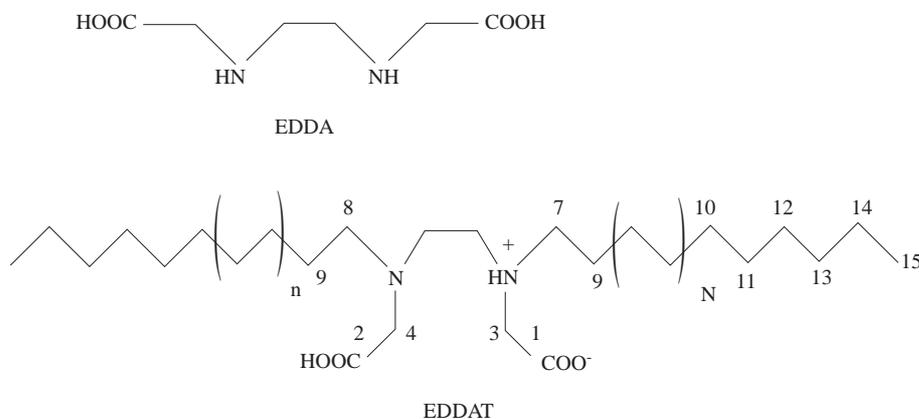
*Standard  $\text{La}^{3+}$  Solution:* A stock solution containing  $1 \times 10^{-2}$  moles  $\text{L}^{-1}$  (M) of  $\text{La}^{3+}$  was prepared by dissolving  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in deionized water. Working solutions were prepared with accurate dilutions.

*Potassium Chloride Solution:* 80 mL of 0.2 N hydrochloric acid, 250 mL of 0.2 M potassium chloride solution and 670 mL of water were mixed.  $\text{pH} \cong 1.8$ .

*Arsenazo III Solution:* 0.10 g of the reagent was dissolved in 100 mL of 0.01 N hydrochloric acid.

All the reagents were obtained from Fluka or Merck and were used without further purification.

*Synthesis of Ethylenediamine-N,N'-ditetradecyl-N,N'-diacetic acid (EDDAT)*



**Scheme 1**

(10.03 g, 0.057 moles) of Ethylenediamine-N,N'-diacetic acid (EDDA) and (4.56 g, 0.114 moles) of NaOH were dissolved in an ethanol/water (10:3) mixture (130 mL). 1-Bromotetra-decane (31.61 g, 0.114 moles) in 50 mL of n-amylalcohol was added to this EDDA solution. The mixture was stirred and heated for 48 hours. After cooling, the resulting precipitate was filtered and washed with ethanol and then water to give a white crystalline powder with a yield of 9.5 g (30 %). The pure sample was obtained in the form of white powdered crystals, m.p 69-70°C, by repeated recrystallization from 90-95 % ethanol followed by petroleum ether(40-60°C).

Anal. calculated for  $\text{C}_{34}\text{H}_{68}\text{N}_2\text{O}_4$  (EDDAT): C, 71.78; H, 12.05; N, 4.92.

Found: C, 71.98; H, 12.10; N, 4.99.

<sup>1</sup>H NMR Spectrum for EDDAT:  $\delta$  0.89 (t, J=6.81, 6H);  $\delta$  1.27 (bs, 48H);  $\delta$  2.41 (t, J=7.48, 2H);  $\delta$  2.74 (t, J=5.45, 2H);  $\delta$  3.20 (s, 2H);  $\delta$  3.41 (t, J=5.45, 2H);  $\delta$  4.14 (m, 4H)

<sup>13</sup>C NMR Spectrum for EDDAT: 169.20 (C-1); 168.18 (C-2); 65.78 (C-3, C-4); 57.94 (C-5); 57.58 (C-6); 50.11 (C-7); 48.01 (C-8); 32.29 (C-9); 30.03; 30.01; 29.98; 29.94; 29.88; 29.71; 29.57 (C-n); 28.91 (C-10); 27.66 (C-11); 27.17 (C-12); 26.22 (C-13); 23.05 (C-14); 14.45 (C-15)

### Extraction of La<sup>3+</sup> with EDDAT in CH<sub>2</sub>Cl<sub>2</sub>

The extraction experiments were carried out in a specially designed jacketed glass tube. The jacket was connected to a thermostatic water supply at a constant 25°C ±0.1°C. Equal volumes of EDDAT in dichloromethane (10 mL) with 2 × 10<sup>-4</sup> M La<sup>3+</sup> (10 mL) were placed in the jacketed glass tube. The parameters used throughout the experiment were as follows: phase ratio, 1:1; temperature, 25°C; contact time, 15 min; and stirring rate, 1300 rpm. After the extraction was complete, the layers separated naturally after 15 min and the pH of the aqueous layer was measured. NaOH and HCl were used for pH adjustment. The La<sup>3+</sup> concentration remained in the aqueous phase at a certain equilibrium pH value. ([La]) was determined using the Arsenazo III method<sup>14</sup>. The absorbance of the aqueous layer was measured at 653 nm, using a 10 mm glass cell with Arsenazo III solution as a reference. Since the initial concentration of La<sup>3+</sup> ([La]<sub>0</sub>) was known, the percentage of La<sup>3+</sup> extracted into the organic phase (i.e. extraction recovery, R(%)) was calculated according to the following equation:

$$R(\%) = \frac{[La]_0 - [La]}{[La]_0}$$

The experiments were repeated three times and the averages of the data obtained are shown in Tables 1, 2 and 3.

## Results and Discussion

In this study, Ethylenediamine-N,N'-ditetradecyl-N,N'-diacetic acid (EDDAT) was synthesized and used in La<sup>3+</sup> extraction. EDDAT was prepared from ethylenediamine-N,N'-diacetic acid (EDDA) and tetradecyl bromide in a basic n-amylalcohol-ethanol-water solvent system. Due to the long-chain alkyl groups (tetradecyl) and the new functional group ( $\alpha$ -amino carboxyl) of EDDAT, this was a different extracting reagent for La<sup>3+</sup> extraction. The structure of EDDAT was identified with <sup>1</sup>H NMR, <sup>13</sup>C NMR and by examining elemental analysis results.

The extraction behavior of La<sup>3+</sup> with EDDAT was studied with 0.1 M and 0.01 M solutions of the reagents in dichloromethane over a pH range of approximately 3.5-7.9, respectively. As shown in Tables 1 and 2, it seems that both the 0.1 and 0.01 M concentrations of the reagent were effective for the extraction of La<sup>3+</sup>. La<sup>3+</sup> was extracted with EDDAT in a higher pH range and the extraction percentages of La<sup>3+</sup> with 0.1 M and 0.01 M EDDAT were 38-95.8 % and 26-65.5 % at pH 6.6-7.9 and 6.9-7.5, respectively.

**Table 1.** La<sup>3+</sup> Extraction from Aqueous Phase with Equal Volume of 10<sup>-1</sup> M EDDAT in Dichloromethane at 25°C

Equilibrium pH	4.3	5.2	6.3	6.6	6.7	6.8	7.0	7.4	7.5	7.7	7.9
R %	0.1	1.6	3.5	38.1	40.0	55.2	76.0	86.6	88.5	93.5	95.8

**Table 2.** La<sup>3+</sup> Extraction from Aqueous Phase with Equal Volume of 10<sup>-2</sup> M EDDAT in Dichloromethane at 25°C

Equilibrium pH	3.5	4.2	5.0	6.0	6.9	7.3	7.5
R %	0.0	3.5	5.4	12.2	26.0	63.0	65.6

As a general rule, La<sup>3+</sup> extraction is better at high pH levels but care must be taken particularly in the more basic pH range where the hydrolysis of La<sup>3+</sup> begins. With liquid-liquid extraction in the basic pH range, the hydrolysis of La<sup>3+</sup> is a significant complication. Consequently, extraction of La<sup>3+</sup> was carried out in a low pH range and no reagent was used to prevent the hydrolysis of La<sup>3+</sup>.

After extraction, the loaded organic phase containing high concentrations of La<sup>3+</sup> may be brought into contact with an acidic solution, whereby the La<sup>3+</sup> is stripped from the organic phase into the aqueous acidic phase. As can be seen from Table 3, only HCl was used in the stripping process and 79.3 % of La<sup>3+</sup> was recovered in a single stripping stage using a solution of 3.59 × 10<sup>-4</sup> M HCl. When the HCl concentration was increased about 25-fold (1.00 × 10<sup>-2</sup> M HCl stripping solution was used), the La<sup>3+</sup> stripping yield increased only 3 %. It was concluded that a concentration of about 3.6 × 10<sup>-4</sup> M HCl gave the best stripping yield. Due to the fact that La<sup>3+</sup> undergoes partial hydrolysis in the extraction process, stripping was not complete.

**Table 3.** Stripping of loaded EDDAT with different HCl concentrations

Stripping Acid HCl (M)	Aqueous Phase		(ppm) La <sup>3+</sup> Loaded Org. Phase Before Stripping	(ppm) La <sup>3+</sup> in Aqueous Phase After Stripping	Stripping Yield (%)
	Initial pH	Equil. pH			
1.00 × 10 <sup>-2</sup>	1.5	1.5	1.816	1.493	82.2
3.59 × 10 <sup>-4</sup>	3.6	3.8	0.947	0.751	79.3
1.79 × 10 <sup>-4</sup>	3.9	5.2	1.227	0.777	63.3
1.40 × 10 <sup>-4</sup>	3.9	6.4	2.077	0.223	10.7
1.00 × 10 <sup>-4</sup>	4.7	6.9	2.129	0.158	7.4

Extraction conditions of the loaded organic phase:

Volume ratio of 10<sup>-4</sup> M La<sup>3+</sup> to 10<sup>-1</sup> M EDDAT is 1:1.

Equilibrium pH: 6.7 - 7.9

% R: 40.0 - 95.8

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