Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2025, Volume 16, Issue 11, Page 2059-2075

http://www.jmaterenvironsci.com

Solvent extraction and separation of lanthanum/silver using Dicyclohexyl-18-crown-6 (DC18C6), Dibenzo-18-crown-6 (DB18C6) and para-tert-butylcalix[6]arene

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Received *18 Sept 2025,*
Revised *19 Oct 2025,*
Accepted *20 Oct 2025*

Keywords:
- *Lanthanum;*
- *extractant;*
- *speciation;*
- *stoichiometry;*
- *Hofmeister*

Citation: *Abdoul-Rachid C. Y., Ali S. B., Ibrahim N., Sabriye Y., Sule A. (2025) Solvent extraction and separation of lanthanum/silver using Dicyclohexyl-18-crown-6 (DC18C6), Dibenzo-18 crown-6 (DB18C6) and para-tert-butylcalix[6]arene, J. Mater. Environ. Sci., 16(11), 2059-2075*

Abstract: This work presents the extraction of lanthanum La^{3+} ions in nitric media with Dicyclohexyl-18-crown-6 (DC18C6), Dibenzo-18-crown-6 (DB18C6) and para-tert-butylcalix[6]arene. The effect of several parameters was studied. The best extraction efficiency percentage for all extractants reached 90% at 1000 ppm. Under the study hydrodynamic conditions La^{3+}_{aq} and $LaNO_{3\,aq}^{2+}$ speciations were obtained and based on slope analysis methods the stoichiometries of the extracted complexes were $\left[La(NO_3)_3DB18C6\right]_{org}$, $\left[La(NO_3)_3DC18C6\right]_{org}$ and $\left[La(NO_3)_2LH_5\right]_{org}$, respectively for DC18C6, DB18C6 and para-tert-butylcalix[6]arene. The lanthanum ion extraction depends on the counter anion added to aqueous solution containing CO_3^{2-}, $C_6H_5O_7^{3-}$, $S_2O_3^{2-}$, CH_3COO^-, and Cl^- was in accordance with the Hofmeister series. According to the separation factor parameter, the best factor between La(III) and Ag(I) separation was obtained at 500 ppm with DC18C6 (β = 84). The study of the thermodynamics parameters of La(III) extraction with all extractants are non-spontaneous and DC18C6 and para-tert-butylcalix[6]arene complexes are more stable than DB18C6.

1. Introduction

Environmental protection has become a major economic and political issue. Better production and less pollution are the challenges facing industrialists in all sectors (Wu *et al.,* 2022). With the rapid development of modern industry, its activities generate a great deal of waste and release various metals and molecules into the environmental matrix, some of which are toxic to humans and their surroundings. As a result, the environmental risks associated with the development of mining activities are increasingly generating heavy metals such as rare earths, Cd, Pb, Zn, Cr, Hg, Cu, Ni, As, Se (Devi *et al.,* 2014; Han *et al.,* 2023; Mohammadpour *et al.,* 2025).

In Niger, gold and uranium mining activities generate radioactive metallic waste such as molybdenum, zirconium and many others (Chaibou Yacouba *et al.,* 2019). Gold mining also generates waste from ore leaching and cyanidation. As a result, heavy metals such as silver and lanthanides end up in the environment.

As heavy metals are not biodegradable under natural conditions, they tend to accumulate in living organisms, causing various diseases and disorders. In addition, the presence of heavy metal ions in wastewater inhibits the biodegradation of organic pollutants that may be present in the water (Feng *et al*., 2024). The World Health Organization (WHO) and the European Union (EU) do not lay down laws, but provide guidelines for setting maximum permissible concentrations. They not only give risk-based recommendations, but also set a tolerance threshold and a maximum permissible concentration (Galal-Gorchev, 1993; Union European, 2023). Consequently, their concentrations must be reduced to acceptable levels according to WHO standards before they are released into the environment.

To protect the environment, and under pressure from government authorities, industrialists have had to take measures to reduce the quantity and toxicity of industrial waste. This struggle has contributed to the development of techniques linking industrial progress and environmental protection, in order to reduce the effects of various effluents. These techniques include membrane processes, ion exchange, leaching, liquid-liquid or solvent extraction, solid-liquid extraction, adsorption and precipitation (Rani *et al.,* 2020; Bilal *et al.,* 2022).

In this context, liquid-liquid extraction, also known as solvent extraction, has seen an important evolution in these applications (Lanjwani *et al.,* 2024). Solvent extraction is a widely used industrial operation in hydrometallurgy, for the separation, purification and concentration of metal ions. Widely used in the nuclear industry for the processing of uranium and thorium ores and the recycling of irradiated fuels, its development has been extended to the exploitation of poor ores, the recovery of traces of toxic or precious elements from polluted industrial effluents, and the separation of elements with similar chemical properties (Nb -Ta, Ni -Co, W -Mo, Zr -Hf, etc.) (Kiegiel *et al*., 2025). This method is simple, effective, fast and easy to implement.

In metal ion extraction, the choice of the extractant molecule is a key element of the extraction process. Indeed, it must be endowed with high extracting power and possibly be selective towards the targeted metal solute (Manousi *et al*., 2019; Muhammad *et al*., 2024). These compounds, like natural antibiotics (Valinomycin, Nonactin, Monactin, Enniatin, Monensin), display particular complexing properties. Born of the success of work carried out in 1967 by Charles John Pedersen and later by D.J. Gram and Jean Marie Lehn, these macrocycles of primarily oxygenated (ether-crown) syntheses, calixarenes, and spherands by their virtue of selectively complexing a cation among their series counterparts, today have a wide-ranging reputation in supramolecule chemistry and have opened up a new era both in liquid-liquid extraction and also in membrane transport thanks to very high extraction selectivity and sometimes to particular and remarkable properties (Ullah *et al*., 2022). This technique has also undergone significant evolution thanks to the use of extractant molecules such as porphyrins, phthalocyanines, crown ethers, calixarenes and macrocycles in general. More recently, the new class of macrocycles, "calixarenes", has attracted the attention of chemists, and taken an important place in the field of complexation associated with the extraction of metal cations (Morohashi *et al*., 2022). This metal-calixarene relationship is leveraged for tasks such as extracting radioactive waste, developing catalysts, anticorrosion, and creating sensors (Al-Trawneh *et al*., 2015; Konczyk *et al*., 2016; Kaddouri *et al*., 2008; Marcos and Berberan-Santos, 2024; Raid *et al*., 2025; Srinivasan *et al*., 2025).

With this in mind, we investigated the liquid-liquid extraction of lanthanum by dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6) and para-tert-butylcalix[6]arene in various organic diluents. The aim of this study is to determine the optimum conditions for successful extraction.

2. Methodology

2.1 Reagents and apparatus

$La(NO_3)_3\cdot 6H_2O$ was obtained from Merck and $AgNO_3$ from Analar Normapur. The stock of solution of 500 mg/L of lanthanum and silver were prepared by dissolving an appropriate amount of metal salt in deionized water and acidified with concentrated HNO_3 to prevent hydrolysis. Ammonia (NH_3) and nitric acid solution were used to adjust pH of the solutions. CH_3COOH, $CH_3COONa,3H_2O$, HCl, NaCl, NaOH, $Na_2S_2O_3,5H_2O$, $Na_2CO_3,10H_2O$, $Na_3C_6H_5O_7$, KCl, Arsenazo (III), Dithizone, tetrachloro-methane (CCl_4) were provided by Merck and Gatt-Koller.

Dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6) and para-tert-butylcalix[6]arene were produced by Merck and Fluka respectively. Toluene and Diisobutyl Ketone (DIBK) were used as diluent. All chemicals and reagents used in this work were of analytical grade.

JENWAY 6705 monochromatic spectrophotometer was used to measure the concentration of metal ions in aqueous solutions. The mixing of aqueous and organic solutions was carried out with a mechanical shaker.

2.2 The solvent extraction procedure

The aqueous solutions were prepared by dissolving appropriate amounts of lanthanum and silver in acidified solutions. Concentration of DC18C6, DB18C6 or para-tert-butylcalix[6]arene in organic solutions was 10^{-3} M. The extraction experiments were accomplished using the phase ratio of O/A = 1 and temperature of 303 K. Then, 10 mL of aqueous solutions were mixed and shaken for 10 min with 10 mL of organic solutions. The two solutions were separated in a separatory funnel. The stripping experiments were carried out using different concentrations of two acids (nitric and hydrochloric), NaOH and distilled water. For the lanthanum assay, 2 mL acetic acid/acetate buffer solution at pH = 3, 100 µL lanthanum solution and 100 µL Arsenazo (III) solution were used. In pillboxes, 5 mL of dithizone solution in tetrachloromethane (CCl_4) and 5 mL of silver solution were brought into contact to form the dithizone-silver complex.

The concentrations of lanthanum and silver ions in aqueous solutions before and after extractions were determinated at 660 and 645 nm for lanthanum and silver respectively using JENWAY 6705 UV-Visible spectrophotometer.

The distribution coefficient (D) and the extraction percentage (E) were calculated from **Eqn. 1** and **Eqn. 2** respectively:

$$D = \frac{(C_o - C)}{C_o} \qquad \textbf{Eqn. 1}$$

$$E = \frac{D}{D + V_a/V_o} \times 100 \qquad \textbf{Eqn. 2}$$

Where C_o, C, V_a and V_o are the concentrations of metallic ions in aqueous solutions before and after extractions, aqueous and organic solutions volumes respectively.

3. Results and Discussion

3.1 Effect of lanthanum concentration

The variation of the initial La(III) ion concentration on the extraction percentage was studied in the range 50 ppm to 1000 ppm. The other parameters were kept constant. The results presented in **Figure 1** show that extraction percentages for all three extractants increase with increasing metal ion concentration. These extraction percentages reach values of 90% for a concentration of 1000 ppm, illustrating saturation of the complexation sites.

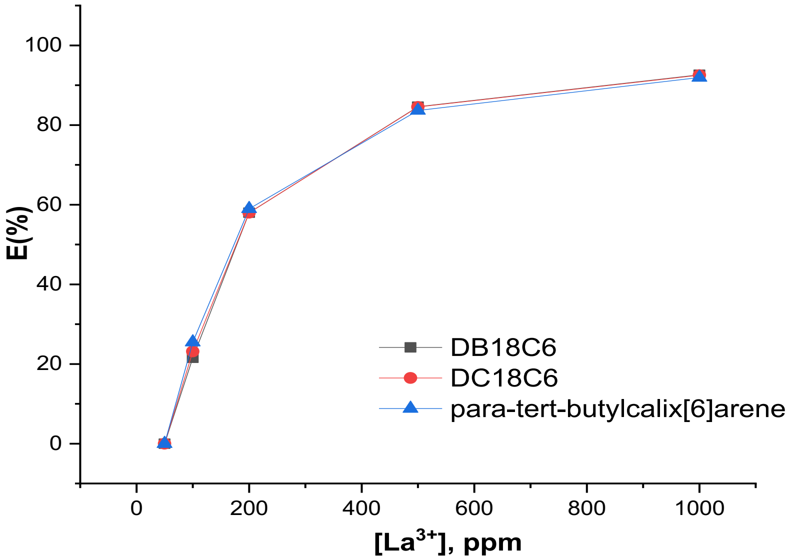


Figure 1. Effect of La(III) concentration on extraction percentage
*([*para-tert-butylcalix[6]arene*]= [DB18C6] = [DC18C6] =* 10^{-3} *mol/L;* $V_{aq} = V_{org} = 10$ *mL;* $pH_i = 3$*; t = 10 mn; T = 303 K)*

3.2 *Effect of initial pH*

The study of the variation of the initial pH of the aqueous phase on the extraction of La(III) ions was carried out by varying the initial pH between 1 and 8 by adding suitable quantities of nitric acid (to lower the pH) and ammonia (to raise the pH) to the aqueous La(III) solution. **Figure 2** illustrates the results obtained. The aim is to increase the extraction percentage for a 100 ppm solution.

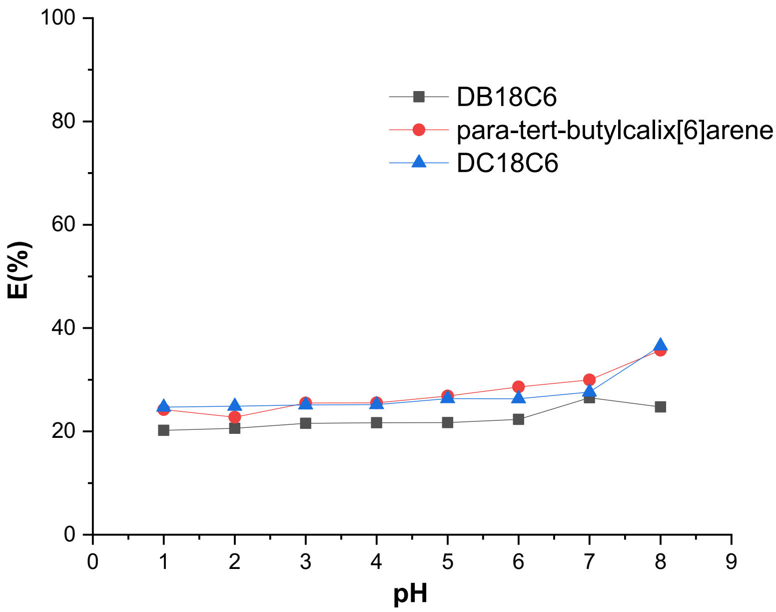


Figure 2. Effect of initial pH on extraction of lanthanum
$V_{aq} = V_{org} = 10$ mL ; $[La^{3+}] = 100$ ppm; [extractant] = 10^{-3} mol/L, t = 10 mn ; T = 303 K

There is a slight increase in the percentage above pH = 3, which would be due to the speciation of lanthanum in aqueous media, as shown in **Figure 3**. The speciation of lanthanum under our hydrodynamic conditions are: La^{3+}_{aq} and $LaNO^{2+}_{3\,aq}$.

At pH = 8, it increases with para-tert-butylcalix[6]arene, and decreases with DC18C6 and DB18C6. This may be due to the low polarity of para-tert-butylcalix[6]arene, which extracts better than DB18C6 and DC18C6, which are neutral. The study of extraction above pH 8 is no longer feasible, as lanthanum is precipitated as $La(OH)_3$ at pH 8 and above. Similar results have been reported on removal of lanthanum and cerium from aqueous solution using chitosan-functionalized magnetite-pectin. (Chaibou Yacouba *et al.*, 2024).

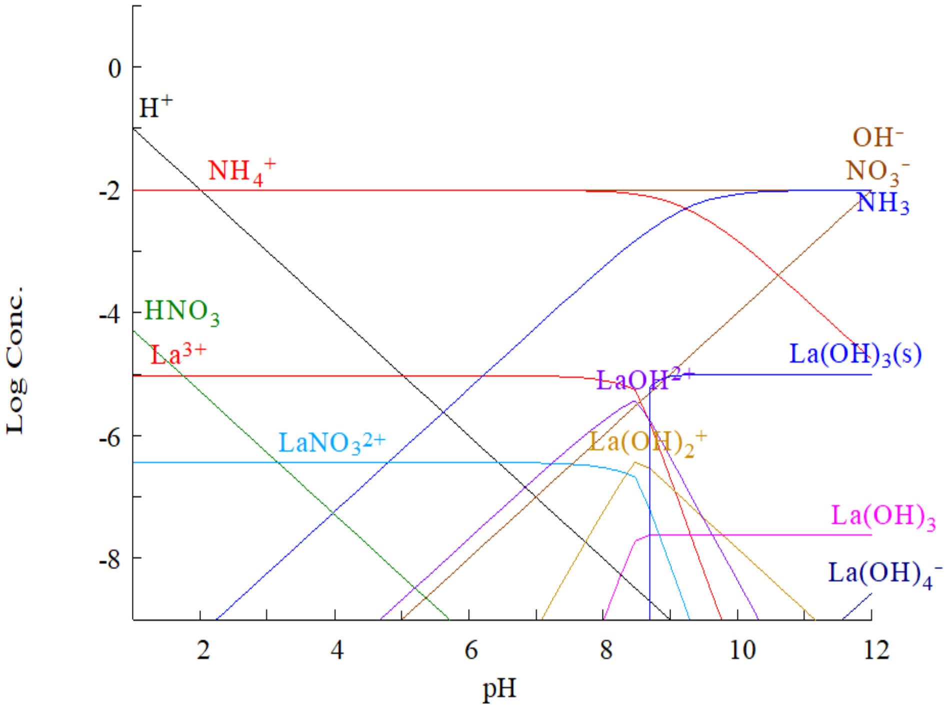


Figure 3. Speciation diagram of $La(NO_3)_3$ solution at 303 K

3.3 *Effect of extractant concentration*

This study focuses on the extraction of La(III) with a concentration equal to 100 ppm, varying the extractant concentrations (para-tert-butylcalix[6]arene, DB18C6, DC18C6) from 10^{-3} mol/L to 10^{-6} mol/L. The results show that the extraction percentage increases only slightly with decreasing para-tert-butylcalix[6]arene and DB18C6 concentration, while it decreases only slightly with decreasing DC18C6 concentration. The study of metal-ligand complexation will provide a better understanding of the extraction process involved. DC18C6 and DB18C6 are solvating extractants, the theoretical equilibrium reactions for the formation of La^{3+} complexes can be illustrated by the following equations:

$$La^{3+}_{aq} + 3\,NO^{-}_{3\,aq} + n\,(L)_{org} \xrightarrow{K} (La(NO_3)_3L_n)_{org} \qquad \textbf{Eqn. 3}$$

where, L is DC18C6 or DB18C6 organic phase, $(La(NO_3)_3L_n)_{org}$ represents the La(III) extractant complexes.

The equilibrium constant, K_{eq}, can then be expressed as follows:

$$K_{eq} = \frac{\left[La(NO_3)_3L_n\right]_{org}}{\left[La^{3+}_{aq}\right]\left[NO^{-}_{3\,aq}\right]^3 L^n} \qquad \textbf{Eqn. 4}$$

with $D = \dfrac{\left[La(NO_3)_3L_n\right]_{org}}{\left[La^{3+}_{aq}\right]}$ **Eqn. 5**

thus, the linearization of the second part of **Eqn. 4** yields:

$$logD = logK_{eq} + 3\ log\left[NO_3^-\right] + n\ log\left[L\right]$$ **Eqn. 6**

finally, the derivatives from both sides of **Eqn. 6** give the estimated values of m as shown by:

$$\left[\frac{\partial logD}{\partial((L)_{org})}\right]_{(NO_3^-)} = n$$ **Eqn. 7**

In order to determine, the n value and the solvent extraction equilibrium reaction, the DC18C6 and DB18C6 concentrations variation in organic solution were studied. The stoichiometry of metal-extractant complexation was graphically determinated by the slope analysis method. As showed in **Figure 4**, the results of variation of DC18C6 and DB18C6 concentrations studies, the extraction percentage efficiency increased by decreasing the DB18C6 concentrations and decreased by decreasing the DC18C6 concentrations. **Figure 4,** also shows the plot of logD versus log[DC18C6 or DB18C6] for lanthanum.

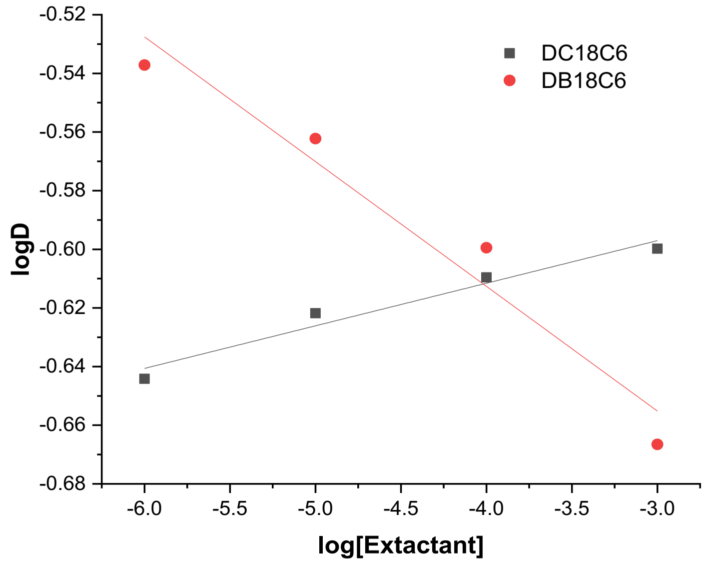


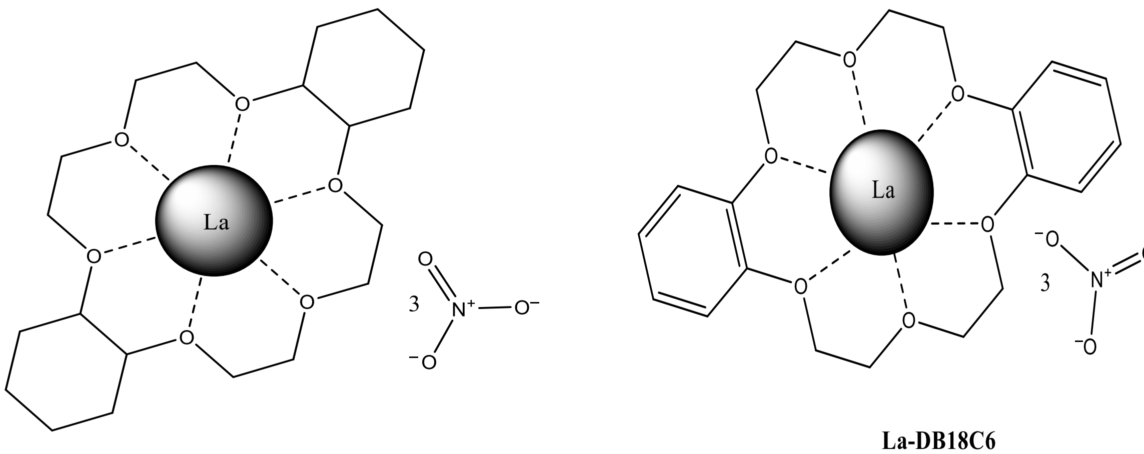
Figure 4. Variation of Log D with Log [DC18C6 or DB18C6] for La(III) extraction. (initial lanthanum concentration: (100 ppm), $pH_i = 6$ and T = 303 K)

The logD increased with DB18C6 and decreased with DC18C6. For both extractant the slope value was slightly 1 and ($R^2 = 0.95$), ($R^2 = 0.97$) for DB18C6 and DC18C6 respectively. Thus, it can be seen that for lanthanum extraction the number of extractant molecules that coordinate the metal was one (n = 1). According to these results, the solvent extraction reactions could be described by the following equations :

$$La^{3+}_{aq} + 3\ NO^-_{3\ aq} + (DB18C6)_{org} \xrightarrow{K} (La(NO_3)_3DB18C6)_{org}$$ **Eqn. 8**

$$La^{3+}_{aq} + 3\ NO^-_{3\ aq} + (DC18C6)_{org} \xrightarrow{K} (La(NO_3)_3DC18C6)_{org}$$ **Eqn. 9**

Therefore, it may be concluded that the complexes formed in the organic solutions were $\left[La(NO_3)_3DB18C6\right]_{org}$ and $\left[La(NO_3)_3DC18C6\right]_{org}$. **The Figure 5** shows the structures proposed for these complexes formed in the organic solutions. Similar structures are reported by (Gil *et al.*, 2022) on the lanthanide single molecule magnet (SMM) complexes based on belt macrocycles studies.



La-DC18C6 **La-DB18C6**

Figure 5. Structure of $\left[La(NO_3)_3DB18C6\right]_{org}$ and $\left[La(NO_3)_3DC18C6\right]_{org}$ complexes

Para-tert-butylcalix[6]arene is an acidic extractant, the theoretical equilibrium reactions for the formation of La^{3+} complexes can be illustrated by the following equation:

$$(La(NO_3)_x)^{n+}_{aq} + m\,(LH_6)_{org} \xrightarrow{K} (La(NO_3)_x\,L(H_{(6-n)})_m)_{org} + n\,H^+_{aq} \qquad \textbf{Eqn. 10}$$

where, $(LH_6)_{org}$ is the Para-tert-butylcalix[6]arene organic phase, $(La(NO_3)_x\,L(H_{(6-n)})_m)_{org}$ represents the La(III)-extractant complex.

Then, the equilibrium reaction constant K_{eq} can be expressed by:

$$K_{eq} = \frac{\left[(La(NO_3)_x\,L(H_{(6-n)})_m)_{org}\right]\times\left[H^+_{aq}\right]^n}{\left[(La(NO_3)_x)^{n+}_{aq}\right]\left[(LH_6)_{org}\right]^m} = \frac{D\left[H^+_{aq}\right]^n}{\left[(LH_6)_{org}\right]^m} \qquad \textbf{Eqn. 11}$$

$$\text{with}\quad D = \frac{\left[(La(NO_3)_x\,L(H_{(6-n)})_m)_{org}\right]}{\left[(La(NO_3)_x)^{n+}_{aq}\right]} \qquad \textbf{Eqn. 12}$$

thus, the linearization of second part of **Eqn. 11** gives:

$$\log D = \log K_{eq} + m\log\left[(LH_6)_{org}\right] + n\,pH \qquad \textbf{Eqn. 13}$$

finaly, the derivate from both side of **Eqn. 13** give m and n estimated values as show by:

$$\left[\frac{\partial \log D}{\partial pH}\right]_{((LH_6)_{org})} = n \qquad \text{and} \qquad \left[\frac{\partial \log D}{\partial((LH_6)_{org})}\right]_{(pH)} = m \qquad \textbf{Eqn. 14}$$

In order to determine, the m, n values and the solvent extraction equilibrium reaction, two factors were studied. The effects of initial pH of aqueous solution and the para-tert-butylcalix[6]arene concentration variation in organic solution. The stoichiometry of metal-extractant complexation was also graphically determinated by the slope analysis method. As illustrated, the results of pH_{eq} and variation of para-tert-butylcalix[6]arene concentrations studies, the extraction percentage efficiency increased by increasing the pH and decreasing the para-tert-butylcalix[6]arene concentrations. **Figure 6** shows the plot of logD versus pH_{eq} of the extracted aqueous solution. The logD increased linearly as the initial pH of aqueous solutions increased, in which the slope value was slightly 1 ($R^2 = 0.96$).

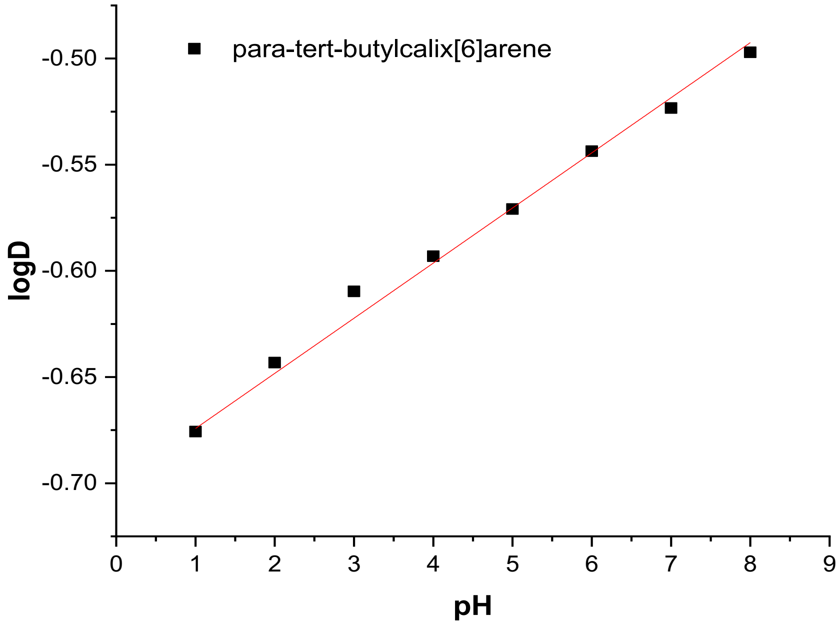


Figure 6. Variation of Log D as a function of pH_{eq} for La(III) extraction
(initial lanthanum concentration: (100 ppm), [para-tert-butylcalix[6]arene] = 10^{-3} M and T = 303 K)

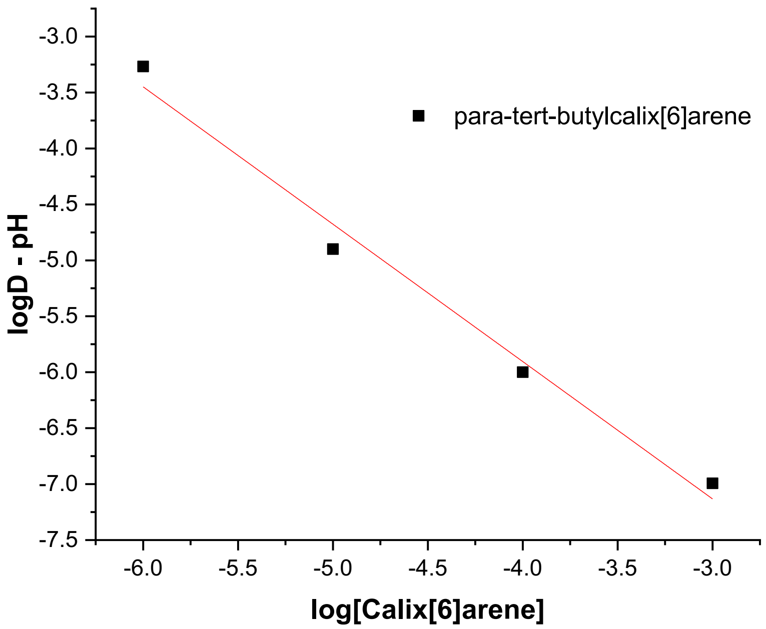


Figure 7. Variation of Log D – pH with Log [para-tert-butylcalix[6]arene] for the extraction of La(III)
(initial lanthanum concentration: (100 ppm), pH_i = 3 and T = 303 K)

Figure 7 illustrates the logD – pH versus log[para-tert-butylcalix[6]arene]. The logD – pH increased in lanthanum extraction as log[para-tert-butylcalix[6]arene] decreased heightened. The slope value was 1.22 (R^2 = 0.98). So, it can be seen that the number of para-tert-butylcalix[6]arene molecule that coordinate the metal was one (m = 1) and one hydrogen ion (n = 1) was released to aqueous phase. According to these results, the solvent extraction reactions could be described by the following equation:

$$(La(NO_3)_2)^+_{aq} + (LH_6)_{org} \xrightarrow{K} (La(NO_3)_2LH_5)_{org} + H^+_{aq} \qquad \textbf{Eqn. 15}$$

Also, it may be concluded that the complexes formed in the organic solutions was and $[La(NO_3)_2LH_5]_{org}$. **Figure 8** shows the structures proposed for the complex formed in the organic solutions. Similar molecule structure is reported by (Hamzi *et al*., 2016) on Lanthanide ion (III) complexes of deprotonated p-tert-butylcalix [n] arene in acetonitrile.

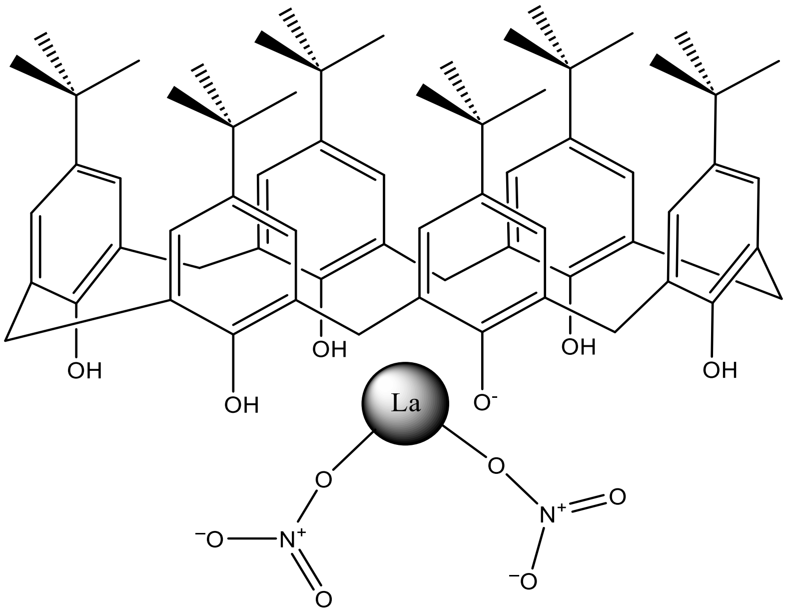


Figure 8. Structure of and $[La(NO_3)_2LH_5]_{org}$ complex

3.4 *Effect of volume ratio*

The effect of varying the volume ratio (V_{aq}/V_{org}) of the two phases on the extraction percentage was studied. The study of this parameter is very important, as it enables us to limit the consumption of organic solvents, which is one of the drawbacks of the liquid extraction technique. The results are shown in **Figure 9**. The best extraction percentages are obtained with the V_{aq}/V_{org} ratio = 0.5, with values of 30.84, 25.49 and 23.31% respectively for para-tert-butylcalix[6]arene, DB18C6 and DC18C6. The better extractability of lanthanum with a V_{aq}/V_{org} ratio = 0.5 would appear to be due to the stoichiometric ratio between the metal and the extractant, the latter of which is higher than that of the metal. Many studies have reported similar results (Song *et al*., 2020), (Tilp *et al*., 2025).

3.5 *Effet of diluant*

The effect of diluent on solvent extraction is a very important parameter. **Figure 10** illustrates the effects of the diluent (toluene and diisobutyl ketone (DIBK)) on the percentage extraction of lanthanum by para-tert-butylcalix[6]arene, DB18C6 and DC18C6.

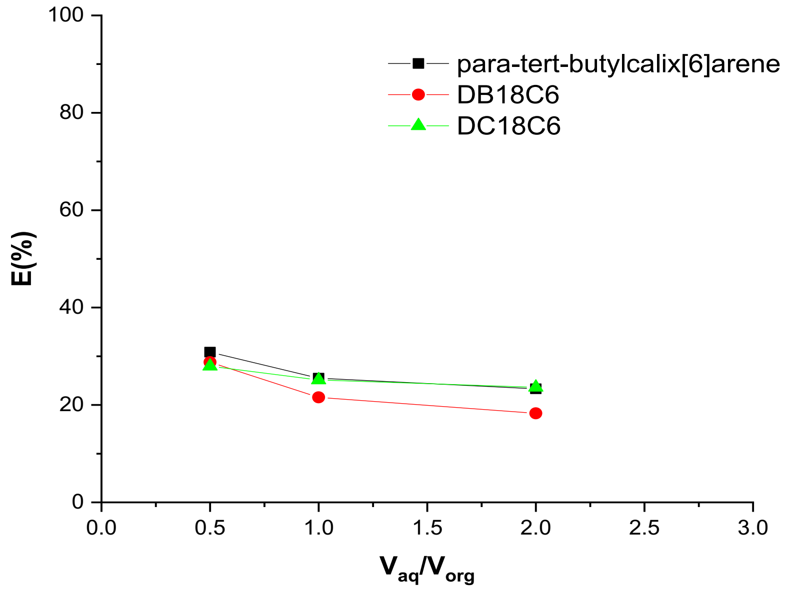


Figure 9. Effect volume ratio on lanthanum extraction
(T = 10mn ; [extractant] = 10^{-3} mol/L ; [La^{3+}] = 100 ppm ; pH = 3 T = 303 K)

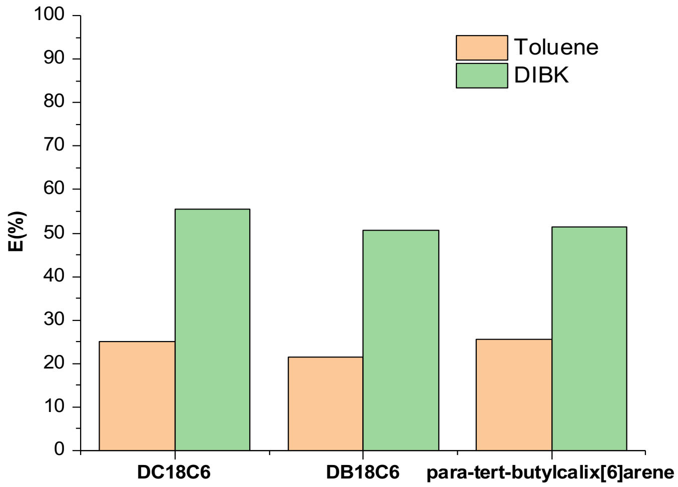


Figure 10. Effect of diluant on lanthanum extraction
$V_{aq} = V_{org}$= 10 mL ; t = 10 mn ; [extractant] = 10^{-3} mol/L ; [La^{3+}] = 100 ppm ; pH = 3 ; T = 303K

Extraction of lanthanum ions is dependent on the nature of the diluent. The different extraction percentage values show that extractability is higher with DIBK than with toluene. DIBK gave an extraction percentage E ≥ 50% with all extractants versus E ≈ 25% with toluene. This result would appear to be due to the difference in dielectric constant (e) between DIBK and toluene. DIBK (e = 9.9), greater than toluene (e = 2.4) illustrates this extractant extractibility with DIBK compared to toluene. Also, the greater the dielectric constant, the greater the solubilizing power of the solvent for cations. This constant also gives the solvent another property, namely polarity: as the dielectric constant increases, so does the polarity of the solvent. (Gerasimov *et al*., 2024) had also deduced that the dielectric constant also indicates that in a more polar solvent, the distribution ratio is higher than in a less polar solvent.

3.6 *Effect of adding salt*

The effect of adding $Na_2CO_3,10H_2O$, $Na_2S_2O_3,5H_2O$, NaCl, $CH_3COONa,3H_2O$, KCl and $Na_3C_6H_5O_7$ at 0.5 M on lanthanum extraction was studied. The results obtained are shown in **Figure 11**. The lanthanum extraction percentage reaches E ≈ 90% in carbonate medium for all extractants, E ≈ 60% in citrate medium for all extractants. Thus, based on the Hofmeister series, the overall order is as follows, $NH_4^+ > K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}$ for cations and $CO_3^{2-} > C_6H_5O_7^{3-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^{2-} > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$ for anions, adding Na_2CO_3, $Na_2S_2O_3$, NaCl, CH_3COONa, KCl and $Na_3C_6H_5O_7$ salts increased the solubilty of the metal complexes. So, the high influence of carbonate ions (CO_3^{2-}) on the extraction showed the salting out behavior. Also, the addition of KCl and NaCl on lanthanum extraction is in agreement with the Hofmeister series for cations with $K^+ > Na^+$ which effectively illustrates the increase in extraction percentage in favor of KCl and showed the salting out behavior. Many authors have reported similar results on the effect of salts as a function of the Hofmeister series (Dupont *et al.*, 2015), (Kang *et al.*, 2020), (Chaibou Yacouba *et al.*, 2023).

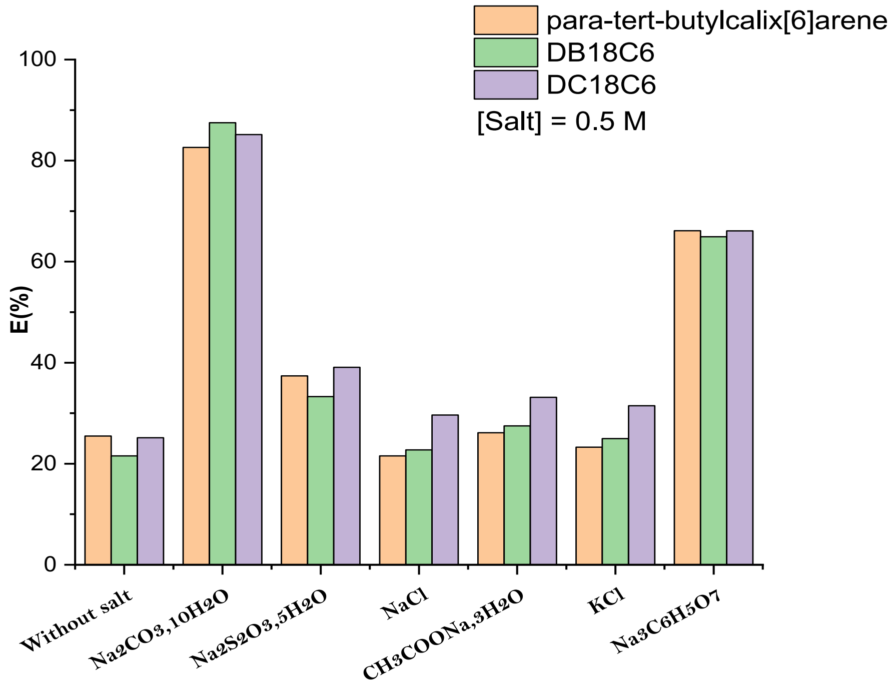


Figure 11. Effect of salt on lanthanum extraction

$V_{aq} = V_{org} = 10$ mL ; t = 10 mn ; [Extractant] = 10^{-3} M ; [La^{3+}] = 100 ppm ; pH = 3 ; T = 303 K

3.7 *Separation factor*

In order to evaluate the optimum conditions for the separation of lanthanum and silver solution the separation factor was studied. The graph of separation factor for separating La(III)/Ag(I) is show in **Figure 12**. The optimum separation factor was obtained at 500 ppm with DC18C6 (β = 84) and at 200 ppm separation factor of β = 60 and β = 58.12 were obtained respectively with DB18C6 and DC18C6. According to HSAB theory, Hard-Soft Acids and Bases are divided in two categories: polarizable or soft and non- polarizable or hard. The principle of this theory says that the hard-hard or soft–soft interactions are stronger than the hard-soft or soft-hard interactions (Pearson, 1963), (Flett, 2005). DB18C6 and para-tert-butylcalix[6]arene can be considered as soft bases due the presence of aromatic phenyl rings and localized electrons. As soft acid, silver ion will prefer to bind with these two extractant. These results facts corroborate the low separation factors observed with para-tert-butylcalix[6]arene. The hard lanthanum behavior strongly interests with a hard base like DC18C6 and this fact explains the high selectivity of lanthanum over silver.

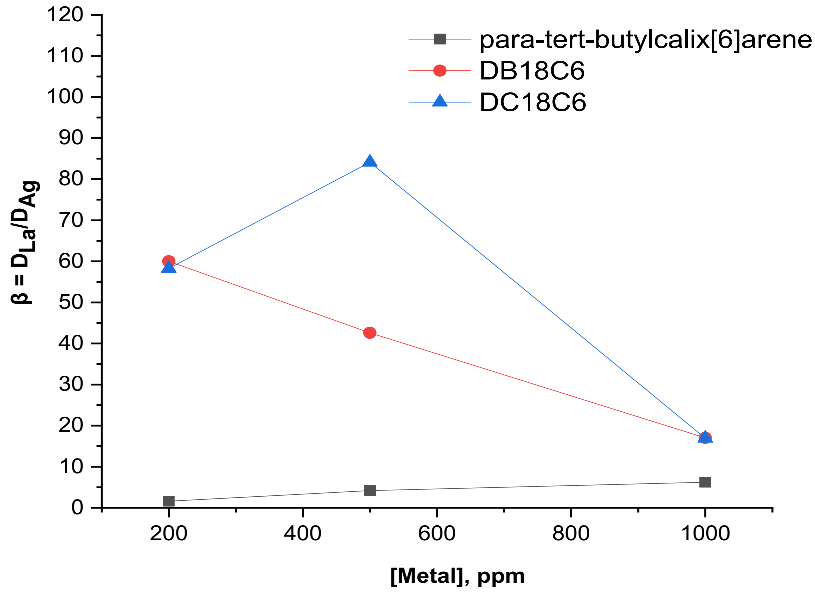


Figure 12. Separation factor of lanthanum and silver extraction with para-tert-butylcalix[6]arene, DB18C6 and DC18C6, $V_{aq} = V_{org} = 10$ *mL; t = 10 mn ;* $[DC18C6] = 10^{-3}$ *mol/L;* $[La^{3+}] = 100$ *ppm; pH = 3; T = 303K*

Based the coordination environment, the ionic size of La^{3+} ion (2.06 Å) is closer to the cavity of DC18C6 (2.2 – 2.8 Å) than DB18C6 (2.6 – 3.2 Å) and para-tert-butylcalix[6]arene (7.6 Å) respectively. This parameter corroborates the stability and high selectivity of La^{3+} ion (2.06 Å) over Ag^{+} ion (1.26 Å). Similar results are reported by several authors (Wenji *et al.*, 1983; Zolgharnein *et al.*, 2003; Maxwell *et al.*, 2018).

3.8 *Effect of temperature*

Temperature is an important parameter in the solvent extraction. In order to explain the thermodynamic behavior of lanthanum ion extraction with para-tert-butylcalix[6]arene, DB18C6 and DC18C6, the experiments were performed at 303 K, 313 K and 323 K. The results indicate that increase at the temperature affect the lanthanum the extraction efficiency. It increased slightly with DB18C6 and decreased slightly with DC18C6 and para-tert-butylcalix[6]arene, which illustrates that DB18C6-La complex is more stable at temperature than DC18C6-La and para-tert-butylcalix[6]arene-La complexes respectively. However, the temperature variation method is often used in solvent extraction to calculate the thermodynamic data of extracted complexes. The standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy (ΔS°) of the complexation and extraction reactions are defined as follows:

$\Delta G° = - 2.303RT\log K_{eq}$ **Eqn. 16**

$\Delta G° = \Delta H° - T\Delta S°$ **Eqn. 17** the change in the equilibrium reaction constant (K_{eq}) with temperature is expressed by the Van't Hoff equation:

$$\log K_{eq} = -\frac{\Delta H°}{2.303R} \times \frac{1}{T} \times \frac{\Delta S°}{2.303R} \qquad \textbf{Eqn. 18}$$

the $\log K_{eq}$ values can be calculated using **Eqn. 6** and **Eqn. 13**, respectively for crown ethers and para-tert-butylcalix[6]arene reactions.

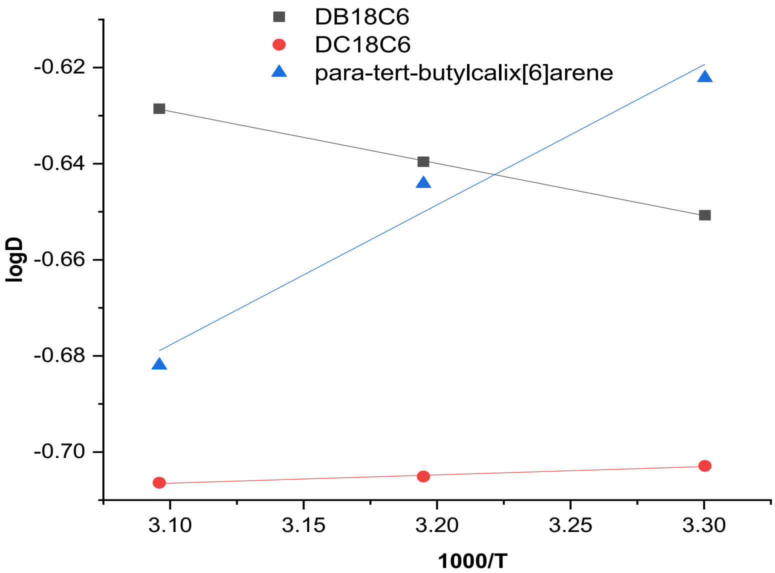


Figure 13. Effect of temperature on lanthanum extraction
$V_{aq} = V_{org} = 10$ mL ; $t = 10$ mn ; [Extractant] $= 10^{-3}$ mol/L ; $[La^{3+}] = 100$ ppm ; pH = 3

The results are shown in **Figure 13**. The plot of log D versus 1000/T shows a good linear relationship. According to the slope and intercept values, the ΔH°, ΔS°, and ΔG° values can be calculated using Equation (11). The thermodynamic values are listed in **Table 1**. ΔG° values of La(III) ion extraction are all positive, indicating that the reaction of La(III) with DC18C6, DB18C6 and para-tert-butylcalix[6]arene are non-spontaneous under these conditions. The positive value of ΔH° of DB18C6 - La(III) complex (2.07 KJ/mol) indicates endothermic reaction, while negative values – 5.58 and – 0.33 KJ/mol of para-tert-butylcalix[6]arene – La(III) and DC18C6 – La(III) respectively indicate exothermic reactions. These results indicate that DC18C6 and para-tert-butylcalix[6]arene complexes are more stable than DB18C6 complex in organic solution. The ΔS° values of La(III) extraction with all extractants are negative. These results indicate a disorder-reducing reaction which may be due to the solvated structure of the complexes formed in the organic solutions. Similar results were reported on the complexation thermodynamics of light lanthanides by crowns ethers (Liu *et al*., 2000).

Table 1. Thermodynamic parameters for the extraction of La(III)

Complexes	$\log K_{eq}$	ΔH°(KJ/mol)	ΔS°(KJ/mol.K)	ΔG°(KJ/mol)
para-tert-butylcalix[6]arene -La	- 10.81	- 5.58	- 0.22	62.71
DC18C6-La	- 0.55	- 0.33	- 0.01	3.19
DB18C6-La	- 0.78	+ 2.07	- 0.01	4.52

Conclusion

In this paper, solvent extraction of La(III) and Ag(I) with DC18C6, DB18C6 and para-tert-butylcalix[6]arene was investigated. The results illustrated that based on the speciation diagram and the slope methods analysis the complexes formed in the organic solution were $\left[La(NO_3)_3DB18C6\right]_{org}$, $\left[La(NO_3)_3DC18C6\right]_{org}$ and $\left[La(NO_3)_2LH_5\right]_{org}$ respectively for DC18C6, DB18C6 et para-tert-butylcalix[6]arene.

A study of the variation in lanthanum concentration showed that the extraction maximum was reached at 1000 ppm with an extraction percentage of 90%. Fixing the concentration of the aqueous phase at 100 ppm to increase extractability, the best conditions were obtained with a volume ratio V_{aq}/V_{org} = 0.5 in polar organic medium with DIBK as diluent. The effect of adding salts to the aqueous solution effectively follows the Hofmeister series, with extraction percentages exceeding 80% for all extractants with $Na_2CO_3.10\ H_2O$. The best separation factor $\beta = 84$ between lanthanum and silver confirmed that the cavity size of DC18C6, DB18C6 and para-tert-butylcalix[6]arene as well as the HSAB theory were major factors governing the nature and stability of metal-ligand complexes. Thermodynamic parameters such as ΔH°, ΔS°, and ΔG° have enabled us to understand the phenomena involved in lanthanum extraction, as well as the stability of the lanthanum. $\left[La(NO_3)_3DC18C6\right]_{org}$ and $\left[La(NO_3)_2LH_5\right]_{org}$ over the $\left[La(NO_3)_3DB18C6\right]_{org}$ complex.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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