Extraction of Cerium using a Synergistic Mixture of Methyl Isobutyl Ketone and Nonylphenoxy Acetic Acid

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Abstract: ***The present work provides a successfully method for selective extraction of cerium from prepared phosphogypsum nitrate leach liquor employing a methyl isobutyl ketone (MIBK), nonyl phenoxy acetic acid (CA100) and a synergism from the two extractants. The extracted complexes of cerium (IV) have been investigated using the slope analysis method. It was found that, cerium was extracted as $Ce\ (NO_3)_3.CA100$, $Ce\ (NO_3)_4.MIBK$ and $Ce\ (NO_3)_2(CA100)_2\bullet MIBK$ by using CA100, MIBK and MIBK-CA100 mixture, respectively. Furthermore, the synergistic effects of the mixed solvents were determined and the maximum synergistic coefficients either the extraction efficiency or the selectivity was obtained at 15 min., 298 K, A/O =1, [MIBK] = 0.1 M/L and [CA100] = 0.5 M/L.***

Keywords: Extraction; Cerium, MIBK; CA100; Synergistic

1. Introduction

In Egypt, the main phosphate industries are responsible in the production of about 20,000 metric tones of phosphogypsum waste per year. Most of this phosphogypsum is disposed as above ground heaps at a rate of 55 kg per day. Phosphogypsum produced during the process is filtered off and drained as slurry to accessible lakes where it stays for a period sufficient to allow complete deposition. However, this waste is then moved to adjoining storage areas it contains minor quantities of trace elements, lanthanides, P_2O_5 and F [1]. An important benefit of Abu-Tartur phosphogypsum lies in their relatively high content of lanthanides (averaging 0.13 %) [2]. Lanthanides and their compounds have gained relevant demands in atomic energy, luminescence, and other industries owing to their characteristic and superior physical and chemical properties [3, 4]. Several programs like solvent extraction, adsorption, and co precipitation, are used to separate lanthanides [5-7].

In this respect, liquid-liquid extraction is widely familiar for separation of lanthanides; the separation feasibility is set by the suitable selection of extractants. Actually, numerous acidic organophosphorus solvents are successfully employed in separation of lanthanides [8, 9]. However, the extraction of lanthanides from waste systems with organophosphorus extractants produces massive amounts of waste water that contains environmental pollutants [10]. Moreover, separation and purification of lanthanides stay troublesome, despite the presence of extractants owing to their similar chemical and physical properties [11]. Thus, developing a brand-new system is important to separate effectively the lanthanides and replaces the common extraction systems [12].

In liquid phases, lanthanides preferentially react with oxygen donors; the bonding is preponderantly electrostatic, and steric factors affect complexation [13]. In this regard, several studies have been manifest that addition of other extractants modifies the organic phase and effectively separates lanthanides [14]. The synergism is caused by the formation of adducts between lanthanides and the solvent, which has been considered due to the displacement of residual coordinated water of the lanthanide chelate by the additional ligand in the organic phase. In past decades, the extraction of metal ions with two types of extractants, has appealed to much investigation. It not only enhances the extraction efficiency but also improves the selectivity significantly [15]. In this consider, the synergistic effect of the mixed solvents have been extensively studied using various β-diketones and neutral organic ligands such as phosphates, phosphine oxides and quinolines for extraction of lanthanides. In the contrary, Carboxylic acids were rarely used for extraction of lanthanides [16-19]. Sec-nonylphenoxy acetic acid (CA100), a novel organic carboxylic acid solvent has several utilities, including low solubility and stronger acidity in aqueous phase. Sun et al. have reported the synergistic effect of bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) and CA100 for extraction of lanthanides with mixtures [20].

In the present paper, the solvent extraction of Ce (IV) by mixtures of CA100 and MIBK from the nitrate medium has been investigated. The synergistic extraction coefficient, the mechanism of the extraction and the thermodynamic function ΔH are clearly determined.

2. Experimental

2.1. Reagents

MIBK and CA100 were supplied by Merk Co. Ltd. and J & K Scientific Ltd, respectively. The solvents were used as received and diluted by kerosene until required concentrations. All other reagents were analytical grade and used without further purification.

2.2. Characterization of the Leach Liquor

The studied leach liquor used in this work was obtained from the dissolution of the phosphogypsum waste drive from wet processing of Abu Tartur phosphate ore, Egypt. Where, 50 g of the ground sample (- 80 μm) was leached with 100 mL of 20 % HNO_3 and 2 mL of 5% nonyl phenol ethoxylate for 30 min[21]. The chemical analysis of the obtained leach liquor presented in Table 1.

Table 1: Chemical composition of the obtained leach liquor of phosphogypsum

Components	Conc., ppm
Ca	9700
SO_4	12500
Fe	1050
F	245
P_2O_5	3200
Ti	11
Th	8
U	14
∑REE	1112
Ce	300

2.3 Extraction procedures

The distribution ratios (D) and selectivity factors (β) of the solutes were determined by contacting equal volumes (20 mL) of their aqueous and organic phases (A/O = 1) in a separating funnel (100 mL). All experiments were carried out at a fixed contact time of 15 min., which is sufficient to achieve equilibrium based on preliminary experiments. Following the extraction, the total amounts of lanthanides were determined colorimetrically by Arsenazo III [22]. Ce^{4+} only was determined by titration using ferroin as the indicator [22].

Eqs. (1) And (2) show the expressions for D and β. Meanwhile, Eq. (3) it indicates the expression for the synergistic enhancement coefficient R which determines whether a mixing system yields a synergistic extraction effect; R > 1 indicates synergistic extraction, whereas R < 1 implies antagonism [23].

$$\mathbf{D = (C_o - C_f)\, V_a / C_f\, V_o} \quad (1)$$

$$\mathbf{\beta = D_{Ce}/D_{Ln}} \quad (2)$$

$$\mathbf{R = D_{mix}/\, D_{MIBK} + D_{CA100}} \quad (3)$$

where C_o and C_f are the initial and equilibrium aqueous phase concentrations of Ce^{4+} ions. V_a and V_o are the volumes of aqueous and organic phases, respectively. D_{Ce} and D_{Ln} denote the D for $Ce^{4+}$and total lanthanides, respectively.

3. Results and Discussion

3.1. Effect of MIBK and CA100 concentration on the extraction of Ce (IV)

Two sets of experiments were investigated to study the effect of solvent concentration on the extraction of Ce (IV) with individual extractants of MIBK and CA100 as shown in Fig. 1. It was performed at 1/1 A/O for 15 min. at room temp., it was found that the distribution coefficient, D_{Ce} increases from 0.18 to 2.2 and from 0.08 to 1.1 with the increase of MIBK and CA100 concentration from 0.05 to 0.6 M, respectively. Hence, it could be effectively extracted by these solvents at the experimental conditions (extraction efficiency about 76 %).

Moreover, to understand the structure of the extracted species either by MIBK or by CA100, the plot of log D versus log [extractant] was constructed as showed in figures 2 and 3 give straight lines of the slopes of 1 for both of MIBK and CA100.

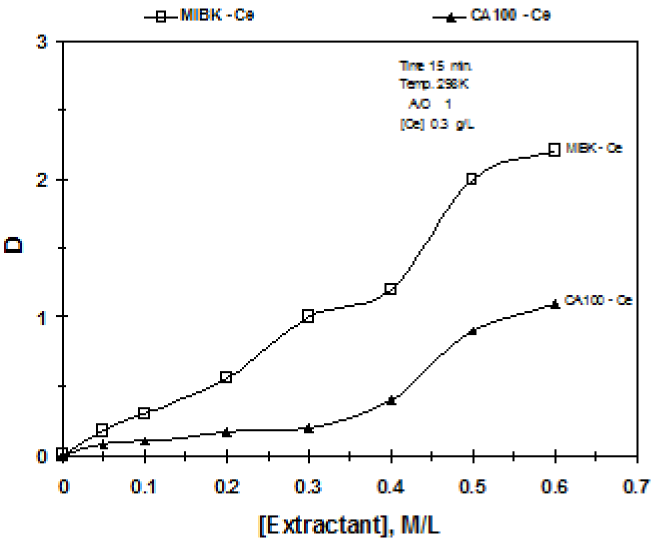

Figure 1: Effect of extractant (MIBK and CA100) concentration on the extraction of Ce (IV) ions

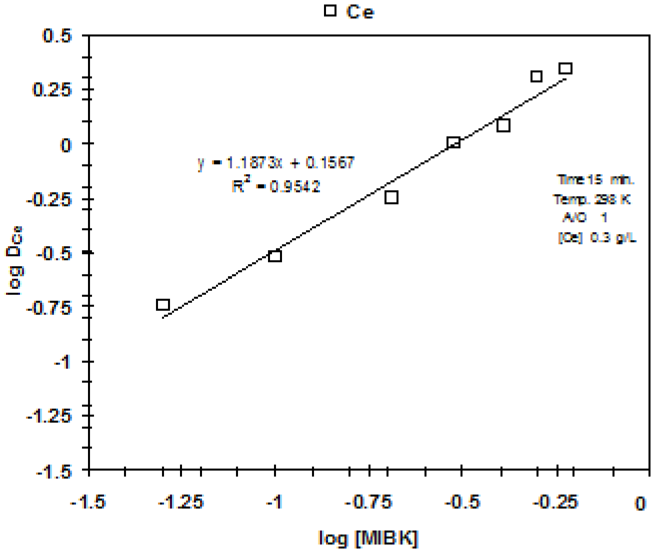

Figure 2: log D of Ce(IV) vs. log MIBK concentration

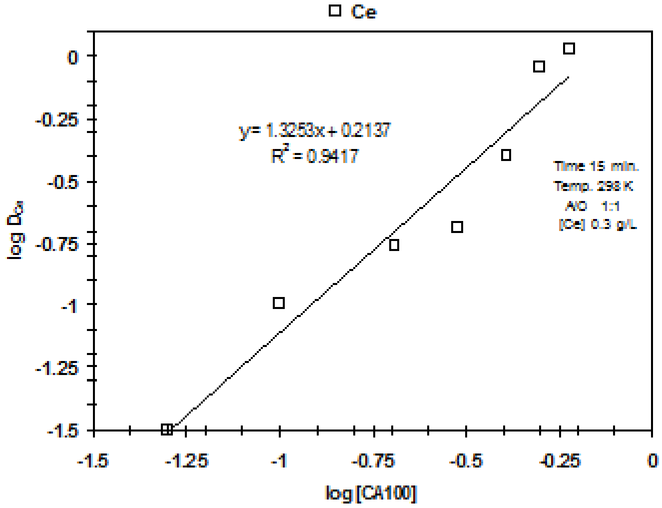

Figure 3: log D of Ce(IV) vs. log CA100 concentration

The extraction equilibrium of Ce (IV) from nitrate media with an acidic CA100 can be expressed as follows [24]:

$$[Ce]^{4+}_{(a)}+3\,NO_3^{-}{}_{(a)}+(CA100)H_{(o)}\rightarrow Ce\,(NO_3)_3\,CA100_{(o)}+H^{+}_{(a)} \quad (4)$$

On the other hand, the extraction equilibrium of Ce (IV) from nitrate media with neutral MIBK is expressed as follows [25]:

$$[Ce]^{4+}_{(a)}+4NO_3^{-}{}_{(a)}+MIBK_{(o)}\rightarrow Ce(NO_3)_4.MIBK_{(o)} \quad (5)$$

3.2. Extraction of Ce (IV) with synergism of MIBK + CA100 solvents

The effect of changing of the MIBK mole concentration on Ce (IV) extraction in the presence of 0.5 M/L CA100 was studied. The obtained results are featured in Fig.4. It indicates that 0.7 M/L MIBK was the effective concentration in the extraction of Ce (IV) from its mixture solutions (D_{Ce} = 90 and E % = 99).

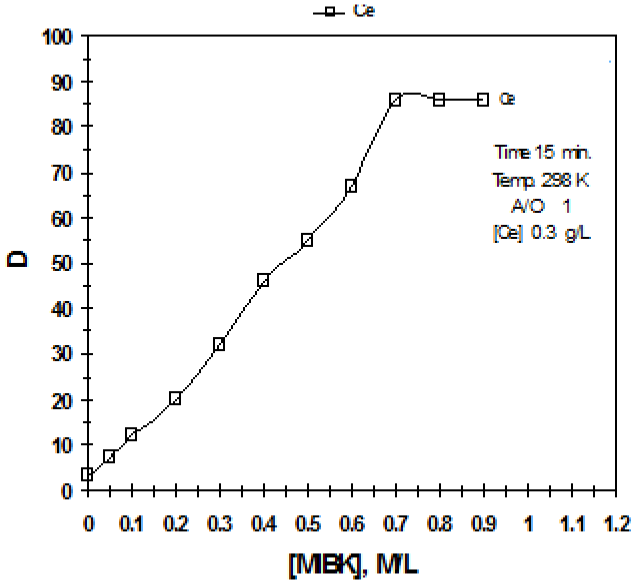

Figure 4: Effect of MIBK concentration on the extraction of Ce (IV) in presence of 0.5 M/L CA100

Plotting the variation of the synergistic enhancement coefficient R with different concentration ratios of MIBK: CA100. Figure 5 showed that the maximum synergistic coefficient value of Ce (IV) equal 26 is obtained at MIBK and CA100 concentrations of 0.7 and 0.5 M/L, respectively.

In order to show the maximum selectivity of two solvents towards the studied element, the relation between the separation factor β and the concentration of MIBK at 0.5 M/L of CA100 is illustrated in Fig.6. It is interesting to note that the selectivity between Ce (IV), and the other lanthanides in the solution varied with a different ratio of MIBK: CA100, and the beta values showed a maximum of 2 at [MIBK] = 0.1 M/L and [CA100] = 0.5 M/L hence. Ce (IV) may be separated, to some extent, from other lanthanides at these concentration ratios of MIBK and CA100.

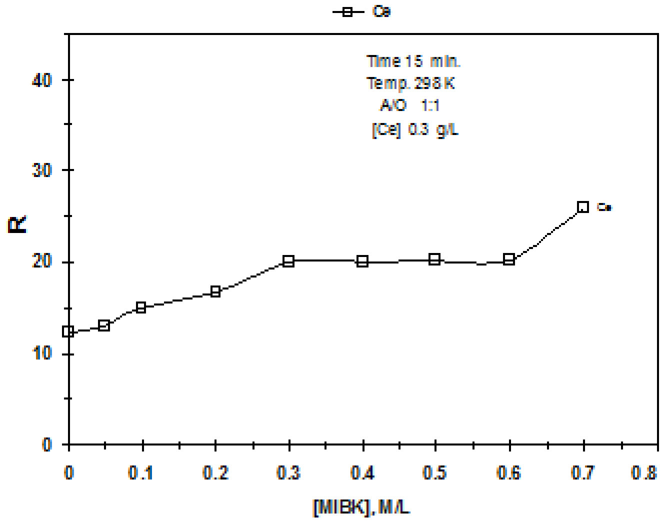

Figure 5: Effect of MIBK concentration on the synergistic enhancement coefficient (R) of Ce(IV) in presence of 0.5 M CA100

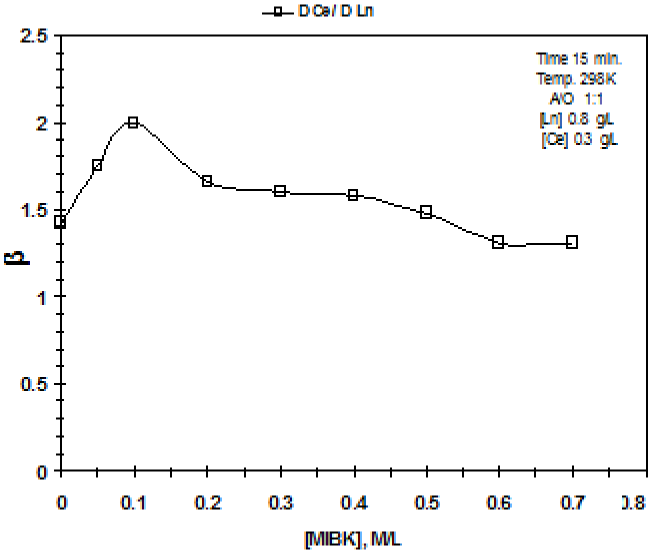

Figure 6: Effect of MIBK concentration on the extraction selectivity (β) of Ce (IV) from other lanthanides (Ln) in presence of 0.5 M CA100

3.3. Mechanism of Ce (IV) extraction with a synergistic mixture of MIBK and CA100

In order to determine the extracted Ce (IV) species in the MIBK + CA100 mixture system, a plotting of log D versus log [HNO_3] at fixed concentration of MIBK and CA100 equal 0.1 M and 0.5 M, respectively was carried out as shown in Fig. 7. This relationship gives a straight line with slope of 4 for Ce (IV), negative value means NO_3^- had been released from the components in the extraction system [26].

Similarly, figures 8 and 9 showed that the relationship between log D_{Ce} and log [extractant] at fixed aqueous acidity was linear with the slope of 1 and 2 for MIBK and CA100, respectively.

According to the above data, the extraction mechanism of Ce (IV) with MIBK + CA100 can be written as follows:

$$\mathbf{Ce\ (NO_3)_{4(a)} + 2(CA100)H_{\ (o)} + MIBK_{\ (o)} \rightarrow Ce\ (NO_3)_2(CA100)_2{\cdot}MIBK_{\ (o)} + 2H^+_{\ (a)} + 2\ NO_3^{\ -}{}_{(a)}} \qquad \mathbf{(6)}$$

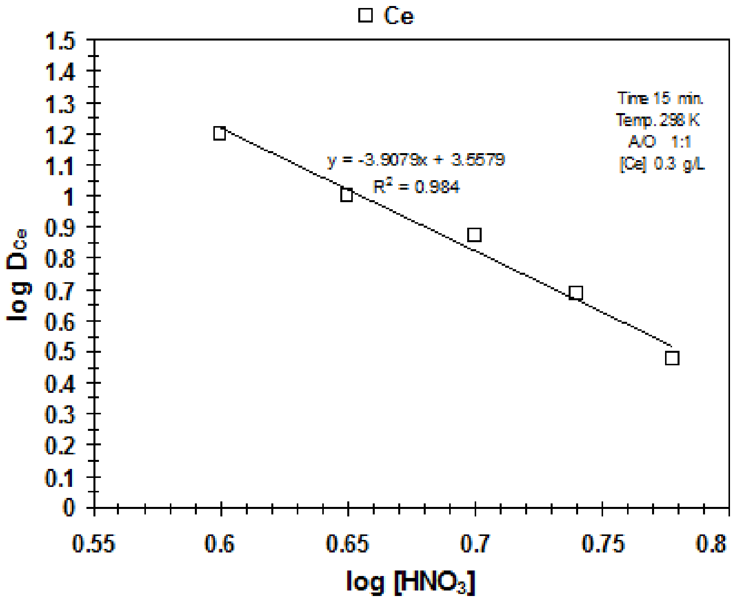

Figure 7: Distribution of Ce (IV) as a function HNO_3 concentration

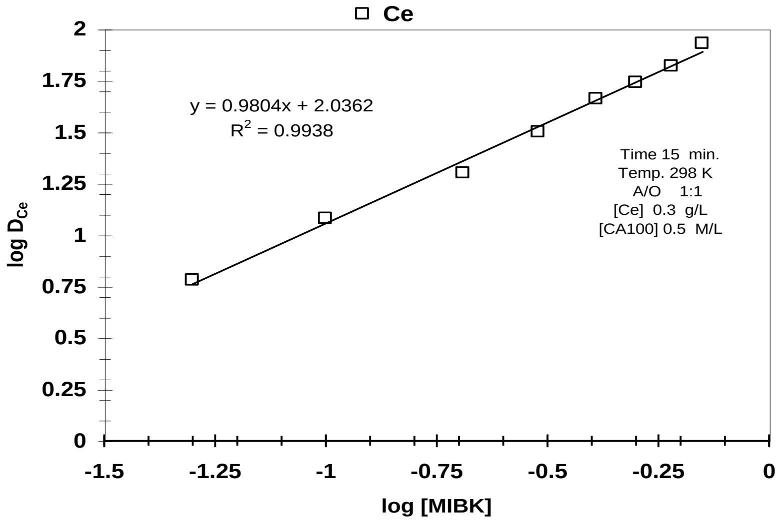

Figure 8: Distribution of Ce (IV) as a function MIBK concentration in presence of 0.5 M CA100

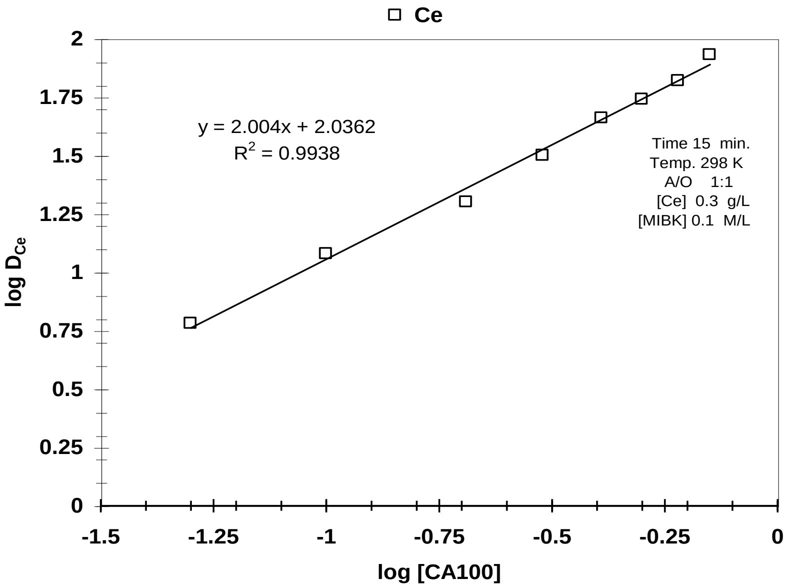

Figure 9: Distribution of Ce (IV) as a function CA100 concentration in presence of 0.1M MIBK

3.4. Effect of temperature on extraction of Ce (IV) with MIBK-CA100 mixture

The effect of temperature of the extraction equilibrium of Ce (IV) was investigated at 4 mol/L HNO_3 concentration. The enthalpy changes during the reaction, ΔH, can be calculated from the slope of the log D versus 1/T as shown in Fig.10 using the Van't Hoff equation as follows:

$$\log D = -\Delta H / 2.303RT + C \qquad (7)$$

where R is the gas constant and C is a constant. The ΔH values are calculated as - 28 KJ M^{1-}. It can be seen that ΔH is a negative value, indicating that the extraction of Ce (IV) by MIBK + CA100 synergistic system is an exothermic reaction.

3.5. Stripping Experiment

An amount of 100 mL containing 0.5 mol L^{-1} CA100 + 0.1 mol L^{-1} MIBK organic phase loaded with 0.3 g/L Ce (IV) has been back-extracted with different concentration of hydrochloric acid. The stripping efficiency versus the concentration of HCl is shown in Fig. 11, indicating that the majority of Ce (IV) can be stripped by only one single stage if the concentration of hydrochloric acid is greater than 0.6 M/L. The chemical composition of the striping solution presented in Table 2.

Table 2: Chemical composition of the obtained striping solution

Components	Conc., ppm
Ca	Nil
SO_4	Nil
Fe	15
F	Nil
P_2O_5	65
Ti	Nil
Th	Nil
U	Nil
∑REE	325
Ce	292

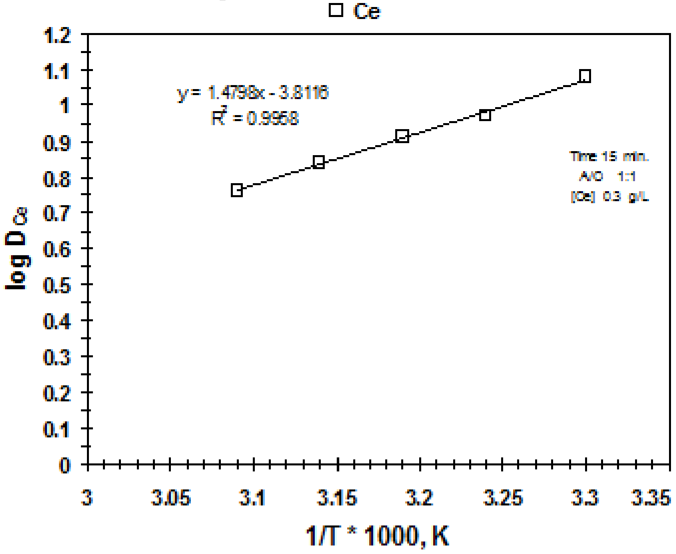

Figure 10: Effect of temperature on the extraction of Ce (IV) by 0.1M MIBK + 0.5M CA100

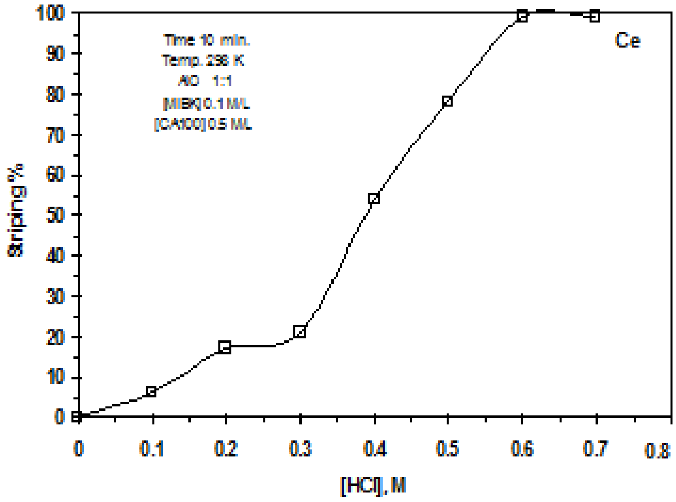

Figure 11: Effect of HCl concentration on striping of Ce (IV) from 0.1M MIBK + 0.5M CA100 mixture

4. Conclusion

The extraction equilibrium of Ce(IV) from nitrate leach liquor of the phosphogypsum with MIBK, CA100 and a mixture of both have been studied, and it was found that:

1) The synergistic enhancement coefficients (R) and the selectivity factors (β) were obtained. Ce (IV) was extracted into the mixed organic phase as Ce $(NO_3)_2 (CA100)_2$MIBK based on the slope analysis method.
2) Ce (IV) can be selectively extracted by using 0. 1M MIBK in presence of 0.5 M CA100, at the optimum conditions of 15 min., A/O 1:1 and room temp.
3) The mixed system has provided an efficient method for separation of Ce (IV). Firstly, we recover total lanthanides from leach liquor using 0.7M MIBK+ 0. 5 M CA100 mixture in kerosene, and then, Ce (IV) can be effectively separated from striping solution by using 0.1M MIBK+ 0.5M CA100 mixture

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