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Extraction of Some Rare Earth Elements (La, Pr and Er) from Citrate Medium Using D2EHPA in kerosene

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Extraction and possible separation of the rare earth elements, REEs, lanthanum (III), praseodymium (III) and erbium (III) from citric acid solution using Di(2-ethylhexyl) phosphoric acid, D2EHPA, in kerosene were studied. The parameters affecting the extraction process were separately studied in order to achieve the maximum possible separation between the different REEs under investigation. It was found that from 1.0 mol/L citric acid solution at pH = 4.0, the extraction is dependent mainly on the citric acid and D2EHPA concentration as well as temperature. From the experimental results and the main species in the aqueous phase, a proposed extraction equilibrium of the different metal ions was given. Conditional extraction constants for the proposed extraction equilibrium were calculated for the different elements, and found to verify the experimental results. The order of the conditional extraction constants follows the sequence, Er (III) >> La (III) ≥ Pr (III). The thermodynamic functions associated with the extraction reaction were evaluated and discussed. Feasibility of separation of Er(III) from La (III), and Pr (III) obtained was given in terms of the separation factors between different elements at different extraction conditions.

Keywords: *Extraction; REEs; Citric acid; D2EHPA; Separation.*

Introduction

Rare Earth elements (REEs) are a group of metals which consists of yttrium and 14 elements of the lanthanides in addition to scandium. The unsaturated 4f electronic structure of lanthanides gives the special properties of the REEs in many fields such as luminescence, magnetism, catalysis, and electronics. REEs have been used in glass polishing, phosphors, batteries, magnets and thermal neutron absorbents. The relatively new applications in the electronics and other industries have resulted to an increased demand for lanthanide materials [1,2]. REEs are generally obtained from minerals as a mixture from which they are separated in groups or as individual elements at varying levels of purity, depending on the use. For the separation purposes, liquid-liquid extraction is one of the main techniques used in industry.

The rare earth elements are extracted and separated from different acid solutions by using different types of extractants including acidic, basic and neutral ones [3-8]. Acidic organophosphorus extractants, such as Di(2-ethylhexyl) phosphoric acid (D2EHPA), were used for the separation of the REEs using solvent extraction technique [9,10]. D2EHPA is one of the acidic extractants which are utilized extensively in the field of f-elements separation. In addition, it has extensive applications in the separation of lanthanides from fission products [11-13].

Solvent extraction of REEs by D2EHPA from various acidic media like hydrochloric, sulfuric

and nitric acid solutions is reported [14-17]. It was found that the extraction of REEs with D2EHPA from hydrochloric acid and sulfuric acid media is the same while it is lower from nitric acid solution. Many efforts were devoted to find out some new extraction systems superior to the current saponified D2EHPA system. Recently, much efforts have been devoted to explore some new extraction systems superior to the current D2EHPA-mineral acid system. Among these, which is more effective includes the introduction of complexing agents into the aqueous phase [18-26]. As early as 1968, Weaver and Kappelmann [27] used a mixture of citric acid and aminopolyacetic acids for preferential separation of lanthanides from actinides without modeling of the extraction mechanism. Toshihiko Ohnuki et al. [28] investigated the chemical states change of lanthanides and actinides in the presence of citric acid solutions. The value of distribution ratio in the presence of citric acid was lower than that in the absence of citric acid, reflecting the formation of Ln(III)-citrate complexes. The results indicated that the presence of organic acids affects the chemical state of lanthanides and actinides. Suneesh et al. [29] investigated the separation between lanthanides and actinides from a mixture of 0.1 M citric acid and nitric acid solution. Yin et al. [30-32] studied the extraction and separation of light rare earth elements using two complexing extraction system based on lactic acid and citric acid with D2EHPA, and the results showed that it could not only improve the extraction efficiency, but also increases the selectivity among some adjacent rare earth elements.

In a previous work, the leaching efficiency of 1.0 mol/L citric acid solution for different lanthanides present in phosphogypsum fertilizer (PGF), was found to be in the order Er (89.4%) > La (81.9%) > Pr (72.0%) [33]. Therefore, the main objective of the present work is directed to study the effects of D2EHPA concentration, pH, contact time, temperature, and phase ratio on the extraction and separation of lanthanum(III), erbium(III) and prasodymium(III) ions from 1.0 mol/L citric acid medium. In addition, extraction equilibrium for different investigated ions was proposed and a conditional extraction constant was calculated for each of the studied metal ions and verified the solvent extraction results.

Experimental

Materials

Stock solutions of La(III), Pr(III) and Er(III) (1.0 g/L) were prepared by dissolving a known amount of the metal oxides produced by Aldrich in a minimum amount of concentrated nitric acid. The solution was evaporated to near dryness, washed with double distilled water (d.d.w) until it became almost free from nitrate ions, then completed to one liter with d.d.w. Required concentrations of the investigated metal ions were prepared from the stock solutions by dilution. Citric acid is a weak organic acid that has the chemical formula $C_6H_8O_7$. The extractant D2EHPA which was purchased from Aldrich is a viscous liquid with the formula $(C_8H_{17}O)_2PO_2H$, a specific gravity of 1.038 g/cm^3 and molecular weight of 322.4 g/mol. It is insoluble in water but exceedingly soluble in organic solvents. The odorless non-aromatic kerosene was used as a diluent for the extractant and obtained from Misr Petroleum Company, Egypt. The total lanthanide concentrations in the studied samples were determined spectrophotometrically by the Arsenazo III method [34]. Individual element in their mixture was determined by ICP-OES. All other reagents were used as supplied without further purification.

Extraction Procedure

Solvent extraction was performed by shaking equal volumes (5.0 ml), unless otherwise given, of aqueous and organic phases until equilibrium in glass tubes using a water-thermostat shaker of the type G.F.L 1083, Germany at 298±1 K. After extraction, the aqueous and organic phases were separated completely using a centrifuge. The concentration of rare earth ions in the aqueous phase was determined spectrophotometrically using a UV-visible spectrophotometer model Shimadzu, UV-160A, Japan. The concentration of the rare earth ions in the organic phase was obtained by mass balance. The distribution coefficient (D), extraction efficiency (%E) and separation factor (SF) were calculated from the following equations:

$$D = \frac{[C]_t - [C]_a}{[C]_a} \tag{1}$$

$$\%E = \frac{100\,D}{D + (V_{aq}/V_{org})} \tag{2}$$

$$SF = \frac{D_1}{D_2} \tag{3}$$

Where, $[C]_t$ is the original metal concentration in the aqueous phase before extraction, $[C]_a$ is the metal concentration in the aqueous phase after extraction, V_{aq} is the volume of the aqueous solution and V_{org} is the volume of the organic solution. D_1 and D_2 denote the distribution ratios of two individual rare earth metal ions.

Results and Discussion
Factors affecting the extraction
The different factors affecting the extraction investigated are the effect of shaking time, the pH of the aqueous solution, D2EHPA molar concentration, phase ratio (volume of aqueous (A) over volume of organic phase (O)) and citric acid molar concentration.

Effect of shaking time
The extraction of Er(III), La(III) and Pr(III) from 1.0 mol /L citric acid solution at pH = 4.0 was carried out by shaking equal amounts of the aqueous and organic phases of 0.02 mol/L D2EHPA for different time intervals ranging from 5.0 to 60.0 min at 25°C, Figure (1). It is clear that for Er(III), as the time increased from 5.0 to 10.0 min, the extraction efficiency (%E) increased from 80.6% to 93.1%, and remained almost constant up to 60.0 min. In case of other metal ions, as the shaking time increased from 5.0% to 10.0% min, the %E increased from 10.5% to 10.8% and from 8.2% to 9.6% for La(III) and Pr(III), respectively. This is followed by a slight decrease with further increase of shaking time due to possible back extraction of metal ions. Therefore, the used shaking time for extraction of the studied metal ions was fixed at 10.0 min.
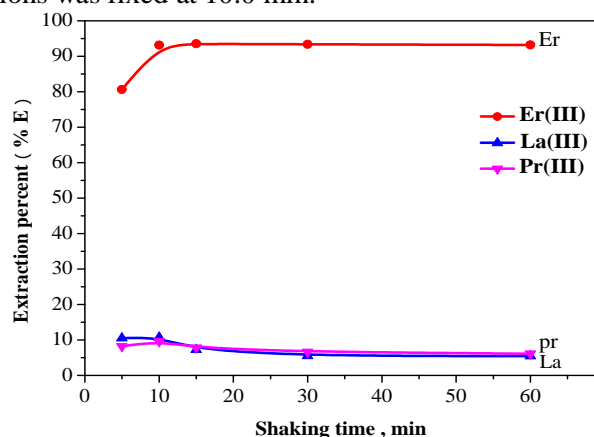

Figure (1): Effect of shaking time on the extraction of Er(III), La(III) and Pr(III) (500 mg/L each) from 1.0 mol/L citric acid solution using 0.02 mol/L D2EHPA in kerosene at pH = 4.0, A/O = 1.0 and 25°C.

Effect of pH
The influence of pH variation on the extraction of the investigated metal ions in 1.0 mol/L citric acid was carried out and presented in Figure (2). The results indicated that for Er(III), as the pH increased from 1.0 to 4.0, the %E increased from 89.4% to 93.1%. In case of other metal ions, as the pH increased from 1.0 to 4.0, the %E increased from around 0.01% to 10.7% and from 1.9% to 10.7% for La(III) and Pr(III), alternatively. The increase in the pH values up to pH 5.0 had a slight decrease of the %E at pH 5.0. This decrease can be related to the possible formation of less extracted hydrolyzed metal ions. Therefore, pH = 4.0 was used as the pH value for further extraction experiments of the investigated metal ions from 1.0 mol/L citric acid solution.
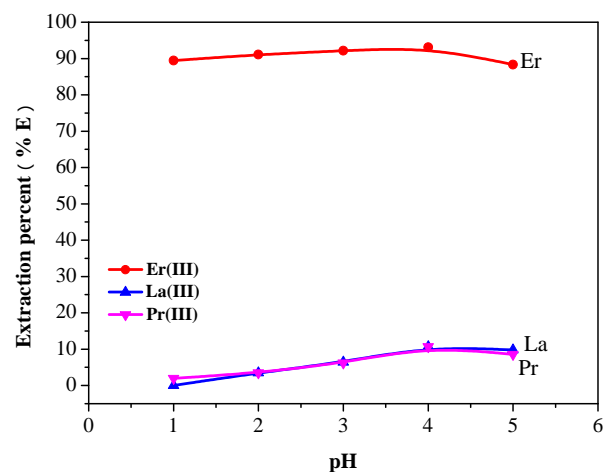

Figure 2: Effect of pH on the extraction of Er(III), La(III) and Pr(III) from 1.0 mol/L citric acid solution using 0.02 mol/L D2EHPA in kerosene at A/O = 1.0 and 25°C.

Effect of D2EHPA concentration
The effect of varying D2EHPA concentration in kerosene in the ranges 0.005-0.08 mol/L on the extraction of 0.5 g/L Er (III), from 1.0 mol/L citric acid medium was studied. In case of La(III) and Pr(III) the change of D2EHPA concentration was within the range 0.02–0.08 mol/L. The obtained results are given in Figure (3). It is clear that the extraction percent increased with the increase in concentration of D2EHPA. Due to that the rare earth ions preferably form extracted complex with D2EHPA. However, 0.02 mol/L D2EHPA was used to enable better separation of Er(III) from other investigated metal ions.
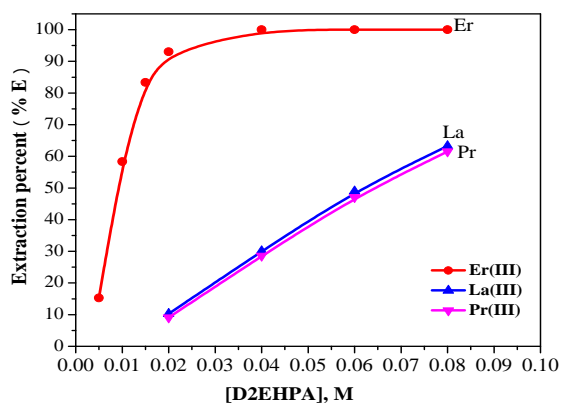
Figure (3): Effect of D2EHPA concentration on the extraction of Er(III), La(III) and Pr(III) from 1.0 mol/L citric acid solution at pH = 4, A/O = 1.0 and 25°C

Effect of phase ratio

The effect of contacting the various volume ratios of aqueous to organic phase on the extraction process was investigated and the results are shown in Figure (4). For Er(III), as the phase ratio increased from 1:1 to 1:6, the extraction efficiency (%E) decreased from 93.5% to 12.5%. In case of La(III) and Pr(III), as the phase ratio increased from 1:1 to 1:4, the %E decreased from 10.90% to 1.48% and from 10.01% to 1.65% for the two metal ions, respectively. This is due to the saturation of the D2EHPA. Therefore, the phase ratio of 1:1 was selected for the extraction experiments.
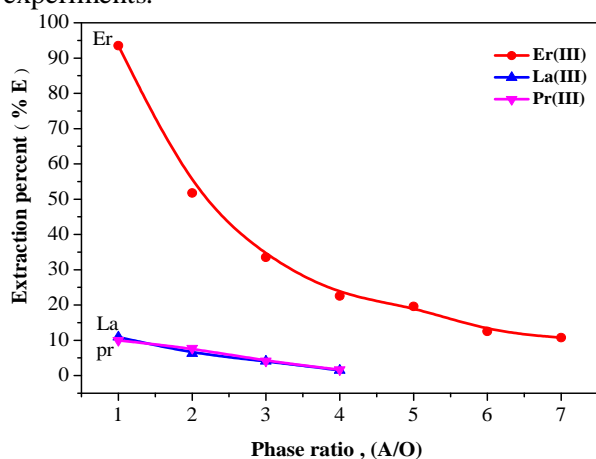

Figure (4): Effect of phase ratio on the extraction of Er(III), La(III) and Pr(III) from 1.0 mol/L citric acid solution using 0.02 mol/L D2EHPA in kerosene at pH = 4.0 and 25°C.

Effect of citric acid concentration

The influence of citric acid molar concentration on the extraction of Er(III), La(III) and Pr(III) (0.5 g/L each) was studied in the citric acid concentration range 0.0–1.5 mol/L using 0.02

mol/L D2EHPA in kerosene. The obtained results indicated that, as the citric acid concentration increases the extraction of metals decreases, Figure (5). The decrease can be related to the possible formation of less extractable metal ions citrate complexes in the aqueous phase.
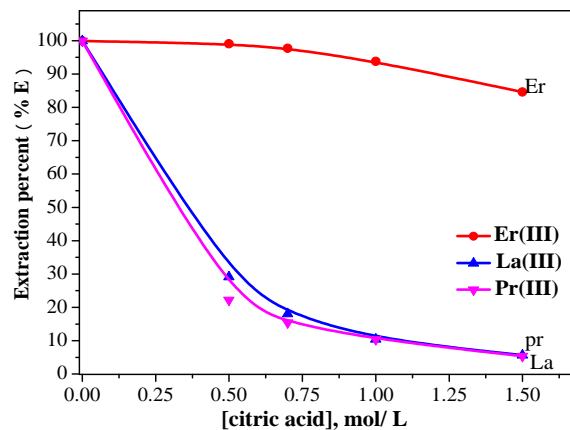

Figure (5): Effect of citric acid concentration on the extraction of Er(III), La(III) and Pr(III) using 0.02 mol/L D2EHPA in kerosene at pH = 4, O:A = 1.0 and T= 25°C.

Modeling of the extraction equilibrium

The aforementioned results indicated that the extraction of the investigated lanthanide metal ions from 1.0 mol/L citric acid at pH 4.0 solution increased by the increase of D2EHPA molar concentration and decreased by the increase of citric acid molar concentration. Further, due to the buffering effect of citric acid, the pH of citric acid solution has limited effect on the extraction for the metal ions investigated. This behavior can be modeled based on the reaction between the main metal cationic ion species at pH 4.0, Ln^{3+}, and the main anionic species of citric acid at the same pH. In this concern, citric acid (H_3Cit) is a tribasic acid with $pK_{a1} = 3.13$, $pK_{a2} = 4.76$ and $pK_{a3} = 6.40$ at 25°C [35]. According to Medusa program (www.kemi.kth.se/medusa), the speciation diagram for 1.0 mol/L citric acid as function of pH is given in Figure (6) [36]. From this figure, more than 77.0 % in the citric acid solution is present as $[H_2Cit]^-$ at pH 4.0. Therefore, it is expected that this species represents the main anionic species responsible for complex formation with the different cationic lanthanide ions investigated. In aqueous solution at pH 4.0, La(III), Pr(III), and Er(III) are present mainly in the free cationic form, [37]. Therefore, we can assume that in 1.0 mol/L citric acid solution at pH 4.0, interaction of $[H_2Cit]^-$ with different trivalent ions (Ln^{3+}) can

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form complexes of the type [Ln(H₂Cit)₃] in solution.

Providing that D2EHPA is a dimer in kerosene [17], and extract cationic species in the organic phase, we can assume that the extraction of the former species will follow the general extraction equilibrium for trivalent lanthanides.

$$Ln(H_2cit)_3 + n(HA)_{2org} \rightleftarrows$$
$$[Ln(H_2cit)_{3-n} \cdot n\,A.(HA)_2]_{org} + nH_3Cit \quad (4)$$
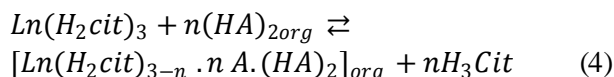
Where (HA)₂ denotes D2EHPA in dimer form.
The conditional extraction constant, $K_{C.ex}$, at 1.0 mol/L citric acid and pH 4.0, is given by the following relation;

$$K_{C.ex} = \frac{\left[Ln(H_2Cit)_{3-n} \cdot n\,A.(HA)_2\right]_{org}\left[H_3Cit\right]^n}{\left[Ln(H_2Cit)_3\right]_{aq}\left[(HA)_2\right]^n} \quad (5)$$

since the distribution ratio is given by;

$$D = \frac{\left[Ln(H_2Cit)_{3-n} \cdot nA(HA)_2\right]_{org}}{\left[Ln(H_2Cit)_3\right]_{aq}} \quad (6)$$

The conditional extraction constant, $K_{C.ex}$, 1.0 mol/L citric acid at pH 4.0, is given as:

$$K_{C.ex} = \frac{D\left[H_3Cit\right]^n}{\left[(HA)_2\right]^n} \quad (7)$$

After linearization and arrangement,
Log D = Log $K_{C.ex}$ + nLog [(HA)₂]- nLog[H₃Cit] (8)

Therefore, it is expected that the relation between log D against log (HA)₂ will give a linear relation with positive slope equals to (n) and the slope of log D against log (H₃Cit) will give a linear relation with negative slope of (n). It is to be mentioned again that the effect of hydrogen ion concentration is neglected due to the slight dependency of hydrogen ion due to the buffering action of the high concentrations of citric acid.

The log-log plot between the D2EHPA concentrations and the corresponding distribution ratios, Figure(7), gave linear relations with positive slopes of 3.0, 2.0 and 2.0 for Er(III), La(III) and Pr(III), respectively. This indicates that two dimers are involved in the extracted species for La(III) and Pr(III) except in case of Er(III) extraction where three dimers participates in the extracted metal species. On the other hand, a plot between log D against the citric acid concentrations gives linear relations, Figure (8). The slopes of these lines were found to be -3.0, -2.0 and -2.0 for Er(III), La(III) and Pr(III), respectively. This indicates that two moles of citric acid is released in the aqueous medium during the extraction of La(III) and Pr(III) while in case of Er(III) three moles of citric acid are released in the aqueous medium during the extraction. These results support the general equilibrium given in equation (4). Subsequently, the proposed main trivalent Ln extracted cationic species in the organic phase from 1.0 mol/L citric acid solution at pH 4.0 are of the types [La(H₂Cit)]⁺ , [Pr(H₂ Cit)]⁺ and Er³⁺ in the organic phase.
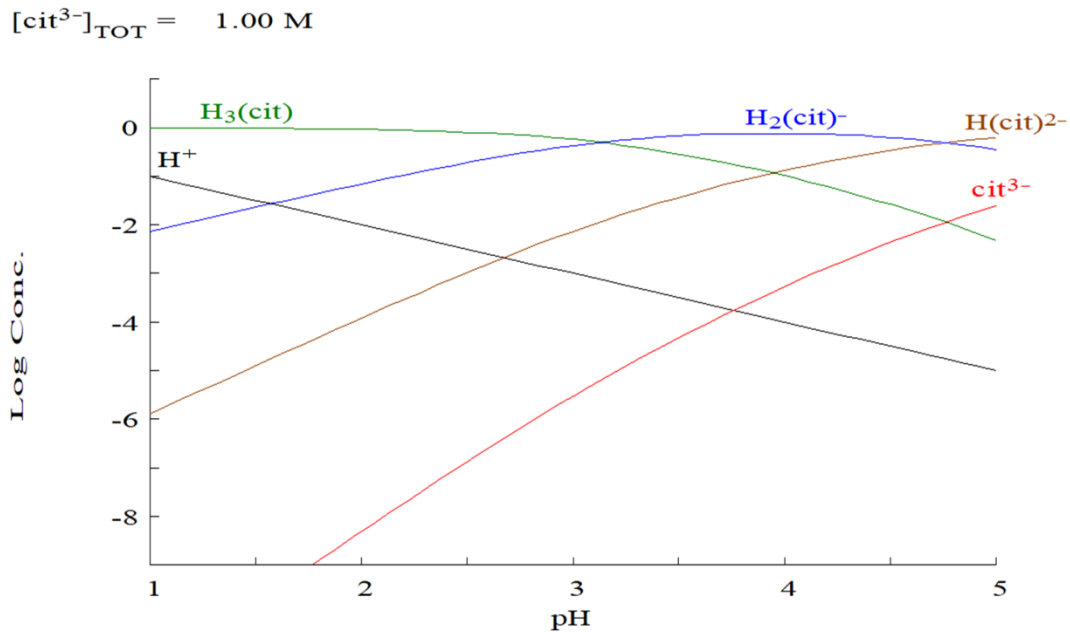
$[cit^{3-}]_{TOT} = 1.00 M$

Figure (6): Equilibrium diagram of 1.0 mol/L citric acid in pH range 1.0 - 5.0.
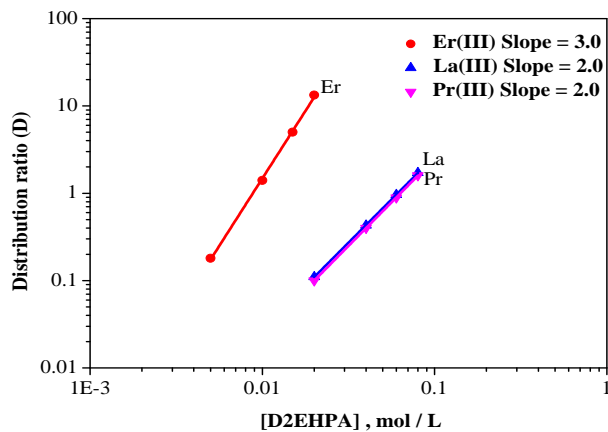(www.kemi.kth.se/medusa)

Figure (7): The log-log linear relationships between the extractant concentrations with the corresponding distribution ratios in the extraction of Er(III), La(III) and Pr(III) from 1.0 mol/L citric acid solution at pH = 4.0, O:A = 1 and 25°C.
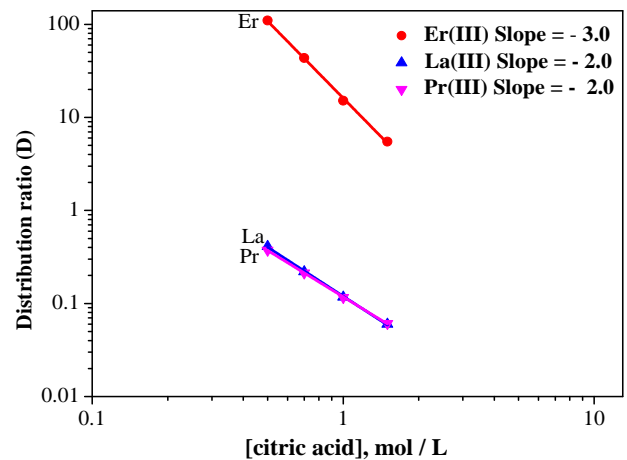

Figure (8): The log-log relationship between the citric acid concentrations and the corresponding distribution ratios in the extraction of Er(III), La(III) and Pr(III) using 0.02 mol/L D2EHPA in kerosene at pH = 4, O:A = 1 and 25°C.

Different values of the conditional extraction constant calculated based on equation (7) at different D2EHPA and citric acid concentrations are given in tables (1 and 2). The mean values of $K_{C.ex}$ for La(III), Pr(III) and Er(III) extraction given in the tables by D2EHPA were found to equal $2.8\pm0.14\times10^2$, $2.7\pm0.23\times10^2$ and $1.72\pm0.32\times10^6$, respectively.

Table (1): Conditional extraction constants $K_{C.ex}$ for Er(III), La(III) and Pr(III) extraction by different concentrations of D2EHPA in kerosene*.

[D2EHPA], mol/L	$K_{C.ex}$		
	La(III) $\times 10^2$	Pr(III) $\times 10^2$	Er(III) $\times 10^6$
0.005	--	--	1.44
0.01	--	--	1.40
0.015	--	--	1.48
0.02	2.75	2.50	1.66
0.04	2.69	2.50	--
0.06	2.67	2.47	--
0.08	2.69	2.50	--
K_{ex} (average)	2.70±0.03	2.49±0.02	1.49±0.12

*1.0 mol/L citric acid at pH = 4.0

Table (2): Conditional extraction constants $K_{C.ex}$ for Er(III), La(III) and Pr(III) extraction by D2EHPA in kerosene at different citric acid concentrations*

[citric acid], mol/L	$K_{C.ex}$		
	La(III) $\times 10^2$	Pr(III) $\times 10^2$	Er(III) $\times 10^6$
0.50	2.57	2.34	1.72
0.70	2.70	2.61	1.86
1.0	2.93	2.90	1.89
1.5	3.38	3.43	2.32
K_{ex} (average)	2.89 ±0.36	2.82 ±0.47	1.95 ±0.26

*0.02 mol/L D2EHPA at pH = 4.0

The distribution ratios for La(III), Pr(III) and Er(III) are calculated from equation (8) at different D2EHPA and citric acid concentrations. The calculated and the corresponding experimental values at different D2EHPA and citric acid concentrations are presented in tables (3 and 4), respectively. There is a great agreement between the experimental and calculated values which supports the proposed extraction mechanism.

Effect of Temperature

The effect of temperature on the extraction of 0.5 g/L of Er(III), La(III) and Pr(III) from 1.0 mol/L citric acid solution by D2EHPA was studied in the temperature range 15–65℃. The obtained results show that by increasing temperature, the extraction percent of the three metal ions decreased, Figure(10). The plot of $\ln K_{C.ex}$ versus 1/T resulted in straight lines for different metal ions, Figure(11). Based on this linear relations, the thermodynamic parameters were calculated from the following relations [38].

$$\ln k_{C.ex} = \frac{-\Delta H}{RT} + C \tag{9}$$

$$\Delta G^o = -RT \ln K_{ex} \tag{10}$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \tag{11}$$

Table (3): The calculated and experimental values of the distribution ratio for Er(III), La(III) and Pr(III) at different D2EHPA concentrations.

[D2EHPA], mol /L	La(III)		Pr(III)		Er(III)	
	$D_{experimented}$	$D_{calculated}$	$D_{experimented}$	$D_{calculated}$	$D_{experimented}$	$D_{calculated}$
0.005	--	--	--	--	0.18	0.215
0.01	--	--	--	--	1.40	1.72
0.015	--	--	--	--	5.01	5.81
0.02	0.11	0.112	0.10	0.11	13.3	13.76
0.04	0.43	0.45	0.40	0.43	--	--
0.06	0.96	1.01	0.89	0.97	--	--
0.08	1.72	1.79	1.60	1.73	--	--

Table (4): The calculated and experimental values of the distribution ratio for Er(III), La(III) and Pr(III) at different citric acid concentrations

[Citric acid], mol/ L	La(III)		Pr(III)		Er(III)	
	$D_{experimented}$	$D_{calculated}$	$D_{experimented}$	$D_{calculated}$	$D_{experimented}$	$D_{calculated}$
0.50	0.411	0.45	0.374	0.43	110.11	110.08
0.70	0.22	0.23	0.213	0.22	43.44	40.12
1.0	0.117	0.112	0.116	0.11	15.33	13.76
1.50	0.06	0.05	0.061	0.05	5.49	4.08

Where, ΔH^o, ΔG^o and ΔS^o are standard enthalpy change, the free energy change, and entropy change, respectively. R is the universal gas constant (8.314 J mole^{-1} K^{-1}), C is a constant and T is the absolute temperature.

From equation (9) and the slope obtained from Figure(10), the standard enthalpy variation (ΔH^o) is obtained. The free energy change (ΔG^o) is obtained by applying equation (10) at standard state, 298 K, and the entropy variation (ΔS^o) is obtained using equation (11); the calculated values are given in Table (5).

The tabuated data showed that the extraction of Er(III), La(III) and Pr(III) is exothermic as indicated by the negative values of ΔH^o. The reaction of the three metals with D2EHPA is spontaneous in nature as shown by the negative sign of ΔG^o values while the positive values of ΔS^o for the three elements show an increase in the randomness of the system during the formation of the extracted species.
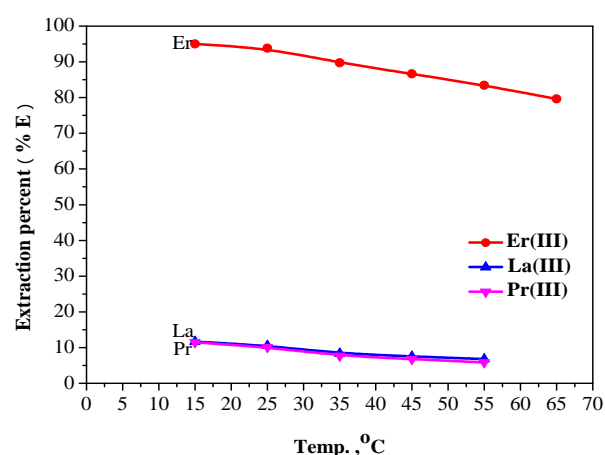

Figure (10): Effect of temperature on the extraction of Er(III), La(III) and Pr(III) with 0.02 mol/L D2EHPA in kerosene from 1.0 mol/L citric acid Solution at pH = 4 and O:A = 1 .

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Table (5): Thermodynamic parameters of the extraction of Er(III), La(III) and Pr(III). from 1.0 mol/L citric acid solution at pH 4.0 by 0.02 mol/L D2EHPA in kerosene at O:A = 1.

Thermodynamic parameter	Er (III)	La (III)	Pr (III)
Enthalpy change (ΔH^o), kJ mole^{-1}	- 9.72	-4.36	- 5.31
Free energy change (ΔG^o), kJ mole^{-1}	-15.56	- 6.12	- 6.07
Entropy change (ΔS^o), J mole^{-1} K^{-1}	19.60	5.91	2.55

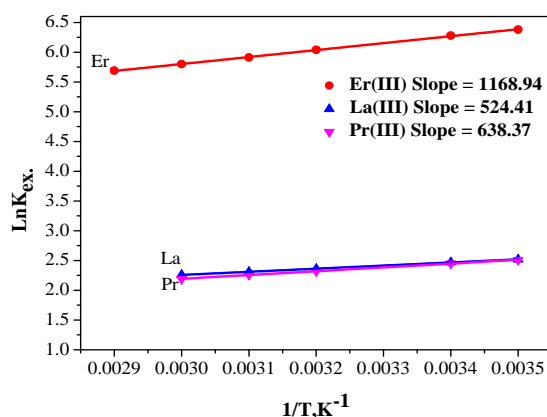**Figure. (11): Relation between (lnK$_{C.ex}$) and (1/T) for the extraction of Er(III), La(III) and Pr(III) with D2EHPA in kerosene from 1.0 mol/L citric acid solution.**

Separation Feasibility

The separation between Er(III) and La(III) is represented by the separation factor (SF) which is given by the ratio of their distribution ratios at equilibrium as follows,

$$SF_{(Er/La)} = \frac{D_{Er}}{D_{La}} \quad (12)$$

Where, D_{Er} and D_{La} are the distribution ratios of Er(III) and La(III), respectively.

From equations 8 the D of Er (III) and La(III) are given as:

$$D_{La} = \frac{K_{C.La}[(HA)_2]^2}{[H_3Cit]^2} \quad (13)$$

and

$$D_{Er} = \frac{K_{C.Er}[(HA)_2]^3}{[H_3Cit]^3} \quad (14)$$

Substituting from equations (14 and 13) in equation (12) gives:

$$SF_{(Er/La)} = \frac{K_{C.Er}[(HA)_2]}{K_{C.La}[H_3Cit]} \quad (15)$$

Substituting with the mean K$_{C.ex}$ values obtained for Er and La :

$$SF_{(Er/La)} = \frac{1.72\times10^6[(HA)_2]}{2.8\times10^2[H_3Cit]} \quad (16)$$

$$SF_{(Er/La)} = 6.14\times10^3 \frac{[(HA)_2]}{[H_3Cit]} \quad (17)$$

Using similar mathematical treatment, the separation factor between Er(III) and Pr(III) can be calculated from the relations:

$$SF_{(Er/Pr)} = 6.37\times10^3 \frac{[(HA)_2]}{[H_3Cit]} \quad (18)$$

The SF$_{(Er/La\ or\ Pr)}$ calculated from equations (17 and 18) depend on the extractant concentration and acid concentration. The plot of the SF against D2EHPA concentration at 1.0 mol/L citric acid, Figure(12), indicates that as the D2EHPA concentration increases, the separation factor between Er (III) and La (III), or Pr(III) increases.

Furthermore, from the plot of the relation between the SF and different citric acid at pH 4.0 and D2EHPA concentrations of 0.02 mol/L, Figure(13), it is clear that as the citric acid concentration increases, the separation factor between Er (III) and La (III) or Pr(III) decreases.

The SF values given by the ratio of their extraction constants and listed in Table 6 show that the separation of Er (III) from Pr(III) or La(III) is in the order: $S_{Er/Pr} > S_{Er/La}$.
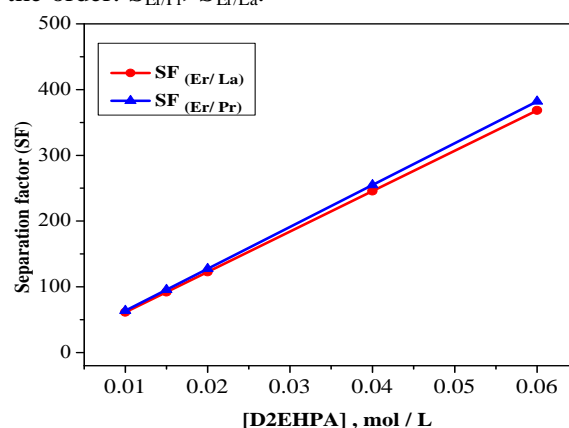

Figure (12): Effect of D2EHPA concentration on the separation factor (SF$_{(Er/La\ or\ Pr)}$) aqueous phase, 1.0 mol /L citric acid solution at pH 4.0.
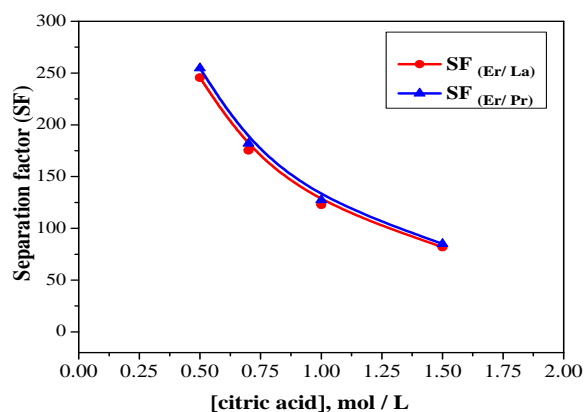
Figure (13): Effect of citric acid concentration at pH 4.0 on the separation factor (SF$_{(Er/La \ or \ Pr)}$) by 0.02 mol /L D2EHPA organic phase .

Table (6): Separation of Er(III), La (III) and Pr(III) extracted from 1.0 mol/ L citric acid solution using 0.02 mol/L D2EHPA in kerosene.

K$_{C.ex}$ (Er)	K$_{C.ex}$ (La)	K$_{C.ex}$ (Pr)
1.72×10^6	2.8×10^2	2.7×10^2
S$_{Er/La}$	S$_{Er/Pr}$	S$_{La/Pr}$
122.8	127.4	1.04

Table (7): Effect of D2EHPA concentration on the separation between Er(III), La(III) and Pr(III).

| [D2EHPA], mol/ L	Separation factors		
	Er/La	Er/Pr	La/Pr
0.02	120.91	133.0	1.1
0.04	--	--	1.08
0.06	--	--	1.09
0.08	--	--	1.08

Based on the separation factors given in tables 6 and 7 it is clear that separation of Er(III) from both La(III) and Pr(III) can be achieved satisfactorily by extraction of Er(III) using 0.02 mol/L D2EHPA from 1.0 mol/L citric acid where by separation of La(III) from Pr(III) is difficult to be achieved under the same conditions.

Conclusion

From the experimental results the following points were concluded:

The extraction of Er(III), La(III) and Pr(III) from 1.0 citric acid by D2EHPA was found to slightly increased by the increase of pH values from 1.0 – 4.0. The extraction of these elements were found to increase by increasing D2EHPA concentration and decrease by the increase of citric acid concentration at pH 4.0. Therefore,

1- The experimental results in terms of D2EHPA concentration in the organic phase and Ln(III) ions in 1.0 citric acid at pH 4.0 in the aqueous phase may give the reaction:

$$Ln(H_2Cit)_3 + n\,(HA)_{2org} \leftrightarrow \left[Ln(H_2Cit)_{3-n}.n\,A.(HA)_2\right]_{org} + n\,H_3Cit$$
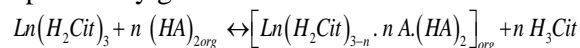
2- The mean species in the organic phase are the following, [La(H$_2$Cit).2A(HA)], [Pr(H$_2$Cit). 2A(HA)] and [Er.3A(HA)], where the cationic complexes of [La(H$_2$Cit)]$^{2+}$ and [Pr(H$_2$Cit)]$^{2+}$ are extracted, while in the case of erpium the free cationic species of Er^{3+} is extracted by D2EHPA.

3- Conditional extraction constant for Er (III), La(III) and Pr(III) extraction by D2EHPA from 1.0 citric acid at pH 4.0 solution was found to follow the order $1.72 \pm 0.32 \times 10^6 \gg 2.8 \pm 0.14 \times 10^2 \geq 2.7 \pm 0.23 \times 10^2$

4- Separation feasibility in terms of the conditional extraction constant indicated that the separation factor of Er(III) from La(III) and Pr(III) increases by the increase of D2EHPA concentration at pH 4.0 and decreases by the increase of citric acid concentration.

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