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**Equilibrium Studies on the Extraction of Yttrium from Chloride Medium by Mono (2-Ethylhexyl) 2-Ethylhexyl Phosphonic Acid (Ionquest 801)**

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**ABSTRACT**

Since <sup>90</sup>Y is one of the useful radioisotopes in nuclear medicine, liquid-liquid extraction of yttrium from chloride medium has been studied under various conditions using neutralized and un-neutralized mono (2-ethylhexyl) 2-ethylhexyl phosphonic acid (EHEHPA) as an extractant. Effect of reagent concentration, pH of the aqueous medium, metal ion concentration and nature of the diluent on the extraction process has been carried out. Effect of temperature was studied and thermodynamic parameters were evaluated. Yttrium extracted in organic phase was stripped with various reagents. The stoichiometry of the extracted species of yttrium was determined on the basis of slope analysis of experimental results. Equilibrium equations of the extraction process have been estimated and verified.

*Key Words: Yttrium / Ionquest 801 / Extraction Constants / Thermodynamic Parameters.*

**INTRODUCTION**

There has been an increase demand for various rare earth elements and compounds particularly high purity rare earth elements and its analogue yttrium <sup>(1)</sup>. Yttrium plays an important role in several commercial applications. It is an important constituent in phosphoresces, catalyst and super conducting materials <sup>(2)</sup>. <sup>90</sup>Y is one of the most useful radioisotopes in nuclear medicine <sup>(3)</sup>.

Liquid-liquid extraction of rare earth elements by several types of reagents has been studied extensively. Owing to their high extraction power and high separation efficiency <sup>(4)</sup>, acidic organophosphorus extracting agents such as di-(2-ethylhexyl)-phosphoric acid (D<sub>2</sub>EHPA) <sup>(5)</sup>, bis(2,4,4- trimethylpentyl) dithiophosphinic acid (Cyanex301), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) <sup>(6)</sup> and bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex302) <sup>(7)</sup>, have been explored for rare earth metals extraction, separation and purification <sup>(8)</sup>. Mono (2-ethylhexyl) 2-ethylhexyl phosphonic acid (EHEHPA) is generally used as an extractant for group separation of rare earths and yttrium <sup>(9)</sup>. Very little information is available on the liquid-liquid extraction and equilibrium process of yttrium using partially neutralized form of these acidic reagents.

Mishra et al <sup>(10)</sup> used an alkyl phosphonic ester named as PC-88A, for simultaneous purification of yttrium and some light rare earths. Ramanujam et el <sup>(11)</sup> separated <sup>90</sup>Y from high level waste by supported liquid membrane based on using an alkyl phosphonic acid named KSM-17 as a carrier. The aim of the present work is to assess the extraction equilibrium of yttrium from chloride medium when extracted with partially neutralized and un-neutralized Mono (2-ethylhexyl) 2-ethylhexyl phosphonic acid (EHEHPA), commercially known as Ionquest 801.

**EXPERIMENTAL**

**Solutions and Reagents**

Mono (2-ethylhexyl) 2-ethylhexyl phosphonic acid (Ionquest 801) kindly supplied by Albright and Wilson Americas was used as received. All diluents and chemicals used are of analytical grade.

Yttrium stock solution was prepared by dissolving an accurately weighed quantity of  $Y_2O_3$  in concentrated HCl solution followed by gentle evaporation till near dryness then washed with distilled water. This washing step was repeated till excess acid was removed. The final residue obtained was dissolved in distilled water to a particular volume.

### **Extraction and Analytical Procedures**

Unless otherwise stated, extraction was carried out with 10 ml of aqueous solution containing 100 mg/l Y(III) equilibrated with equal volume of organic solution containing 0.015 M Ionquest 801 in kerosene. The pH of aqueous solution was initially adjusted at 1.7 by adding HCl and/or NaOH solution before equilibration. The organic and aqueous solutions were mixed and equilibrated at the ambient room temperature ( $25 \pm 1$  °C) by shaking for 15 min. using a thermostated shaker. This time was found enough to attain equilibrium as verified in preliminary tests. After equilibration, the two phases were separated by centrifugation. The loaded organic phase was then stripped back with equal volume of different stripping agents.

Yttrium concentration was measured spectrophotometrically using the UV-visible spectrophotometer (model UV-160 A, Japan) and Arsenazo III as an indicator <sup>(12)</sup>. The concentration was determined from its absorbance at  $\lambda_{max}$  650 nm using the respective calibration graphs. The concentration of Y(III) in organic phase was calculated by the difference between its concentration in aqueous phase before and after extraction. The distribution ratio (D) was defined as:  $D = [Y^{3+}]_{org} / [Y^{3+}]_{aq}$  where  $[Y^{3+}]_{org}$  and  $[Y^{3+}]_{aq}$  are the concentration of yttrium in the organic and aqueous phases at equilibrium, respectively.

## **RESULTS AND DISCUSSION**

Different parameters affecting Y(III) extraction with EHEHPA in its acidic form were studied such as effect of hydrogen ion concentration and extractant concentration. Obtained results showed that extraction of Y(III) by EHEHPA in its acidic form is low and found not to exceed ~ 44%. Therefore modification of extraction conditions by neutralization of the extractant (EHEHPA) was carried out to enhance the extraction process.

### **Effect of Sodium Salts**

Three different methods for sodium salt formation of EHEHPA (neutralized or saponified form) were tested;

- i- Shaking equal volumes of NaOH solutions of different concentrations with 0.015 M EHEHPA in kerosene for 15 min. This organic phase was then used for extraction of yttrium at pH 1.7. The obtained results are given in Table 1. It is clear that the Y(III) extraction increases with the increase in NaOH concentration used for treatment. The neutralized and un-neutralized EHEHPA were titrated with standard NaOH solution using bromocresol purple as an indicator <sup>(11)</sup>. From the

difference in volume of standard NaOH solution used in both cases, the degree of neutralization was evaluated which was found to be 50% at 2 M NaOH solution.

- ii- Forming the salt during the extraction process by shaking equal volumes of the organic extractant (0.015 M) with the aqueous solution of pH 1.7 containing 100 mg/l yttrium and one of the sodium salts (NaCl, Na<sub>2</sub>SO<sub>4</sub> or NaNO<sub>3</sub>). The obtained results are given in Table 2. As shown from the results, addition of sodium salts to the aqueous solution enhances the extraction of yttrium in the following order NaCl > NaNO<sub>3</sub> ~ Na<sub>2</sub>SO<sub>4</sub>. The extraction percentage (%E) of Y(III) reaches maximum (> 95%) using 2 M NaCl solution or more.

**Table 1: Effect of neutralizing Ionquest 801 by different NaOH concentrations on the extraction of Y(III) .**

NaOH Conc., M	%E of Y(III)
0.00	43.85
0.05	70.3
0.10	73.8
0.50	79.9
1.00	80.9
2.00	81.8
2.50	82.2
3.00	82.4

**Table 2: Effect of neutralizing Ionquest 801 by different sodium salts concentrations in aqueous solution on the extraction of Y(III).**

Na salt Conc., M	%E of Y(III)		
	NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>
0.01	85.5	67.0	66.9
0.10	87.2	73.4	72.5
0.50	90.9	79.0	78.0
1.00	93.4	81.7	79.9
1.50	94.7	83.6	81.8
2.00	95.2	86.7	83.7
3.00	95.4	86.7	83.6

- iii- Combining the above two methods, i.e neutralizing EHEHPA with NaOH solution before extraction of Y(III) from the aqueous phase containing each of the above mentioned salts, the results obtained are given in Table 3.

By comparing the extraction percent (%E) obtained by the three methods, it is clear that the most efficient method for the extraction of Y(III) is method iii. But, comparing the %E obtained by methods ii and iii, at the same sodium salt concentration, it was found that, the difference in %E between the two methods does not exceed 2% which is not a significant difference. Therefore, economically, method ii is recommended for the extraction process of Y(III).

#### **Effect of Diluent**

Extraction of Y(III) from chloride medium, 2 M NaCl, of pH 1.7 using 0.015 M EHEHPA in various diluents has been investigated, Table 4. These results show that the

extraction of Y(III) increases as the dielectric constant of the diluent decreases. Accordingly, kerosene was used as a suitable diluent for Ionquest 801 in the following studies.

### Effect of Hydrogen Ion Concentration

The effect of hydrogen ion concentration in the range from  $10^{-6}$  - 0.32 M on the extraction of Y(III) has been investigated, Fig. (1). It is clear that Y(III) extraction increases with increasing hydrogen ion concentration to reach maximum when the hydrogen ion concentration in the aqueous phase is ranged from 0.01 to 0.03 (i.e. at pH from 1.5 - 2.0). This increase can be related to the

**Table 3: Effect of neutralizing Ionquest 801 with 2 M NaOH on extraction of Y(III) from aqueous medium containing different sodium salts concentrations.**

Na salt Conc., M	%E of Y(III)		
	NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>
0.01	86.5	70.6	71.9
0.10	91.5	76.1	76.5
0.50	94.5	82.3	80.6
1.00	95.2	85.4	81.9
1.50	96.4	86.3	83.7
2.00	97.1	87.2	84.9
3.00	97.3	89.1	84.9

**Table 4: Dependence of Y(III) extraction by EHEHPA on the nature of diluent.**

Diluent	Dielectric constant ( $\epsilon$ )	D	%E
Methylisobutyl ketone (MIBK)	13.11	0.13	11.50
Chloroform	4.90	0.55	35.48
Ethyl benzene	3.00	1.67	62.55
Xylene	2.26	6.37	86.43
Toluene	2.24	6.82	87.21
Carbon	2.21	7.68	88.48
Cyclohexane	2.02	11.58	92.05
n-hexane	1.90	14.79	93.76
Kerosene	1.80	22.26	95.70

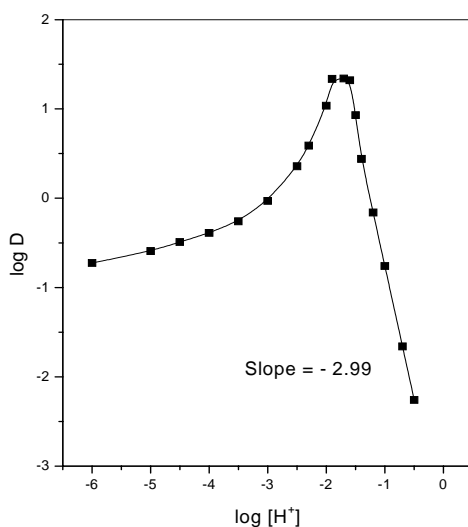
transformation of the hydrolyzed yttrium cationic species, such as  $Y(OH)_2^+$  and  $Y(OH)^{2+}$  to the free trivalent cationic species Y(III), which is highly extracted. With further increase in acidity of aqueous medium, the hydrogen ions in solution compete with yttrium for the extractant with subsequent decrease in its distribution ratio. In the hydrogen ion concentration range 0.02 – 0.32 M, the log–log plot of hydrogen ion concentration in aqueous phase vs. the corresponding distribution ratios, D, of Y(III) gave a straight line with a negative slope of around 3. This indicates that extraction of Y(III) from chloride medium follows the usual cation exchange mechanism. The acidity dependence of 3 also indicates that yttrium (III) is fully neutralized by anionic species of the reagent in organic phase; where further yttrium is extracted mainly as free Y(III) ions.

### Effect of Chloride Ion Concentration

In spite of rare earth ions (III) are very unlikely to complex with chloride ion <sup>(1)</sup>, it was reported <sup>(5)</sup> that chloride ions can be coordinated to the extracted complexes of rare earths under some experimental conditions. In order to investigate if the chloride ions take part in the extraction reaction, the effect of chloride ions on the extraction equilibrium was performed using different concentrations of different chloride salts at constant Y(III) concentration (100 mg/l) at pH 1.7 using 0.015 M extractant neutralized with 2 M NaOH. The obtained results presented in Table 5 show that changing chloride ion concentrations in both NH<sub>4</sub>Cl and KCl has no effect on %E of Y(III). On the other hand, changing of NaCl concentration shows an increase in %E with increasing NaCl concentration. This means that Na<sup>+</sup> ions have a selective effect on the extraction process.

### Effect of Extractant Concentration

Extraction of yttrium was carried out by varying EHEHPA concentration from 0.001 to 0.15 M dissolved in kerosene. The obtained results showed that extraction of Y(III) increases with increasing extractant concentration and reaches maximum at 0.04 M (~ 100 %). Plot of the log-log relation between EHEHPA concentration (in the concentration range from 0.001-0.04) and the corresponding distribution ratios, D, a straight line with slope of ~ 3.0 is obtained, Fig. (2). This inferred that three dimeric molecules of EHEHPA are involved in the extracted complex of Y(III).



**Fig. (1): Effect of hydrogen ion concentration on the extraction of yttrium (100 mg/l) from 2 M NaCl, by 0.015 M neutralized Ionquest 801 in kerosene at 25 ± 1 °C.**

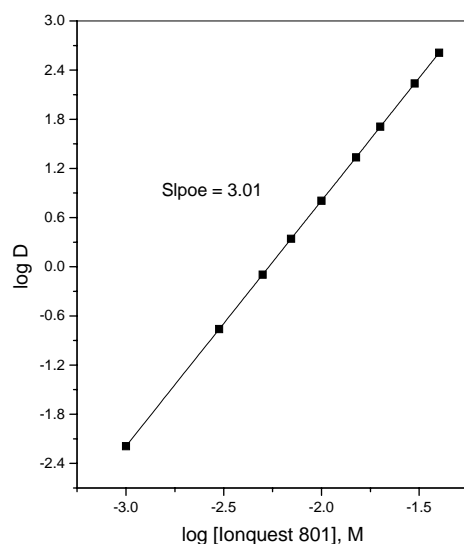
**Table 5: Effect of chloride ion concentration on the extraction of Y(III) by 0.015 M Ionquest 801.**

Cl <sup>-</sup> Conc., M	%E of Y(III)		
	NaCl	NH <sub>4</sub> Cl	KCl
0.05	88.7	82.3	80.7
0.10	91.5	81.8	81.5
0.50	96.5	81.9	82.4
1.00	96.9	83.0	80.9
1.50	97.1	82.7	80.8

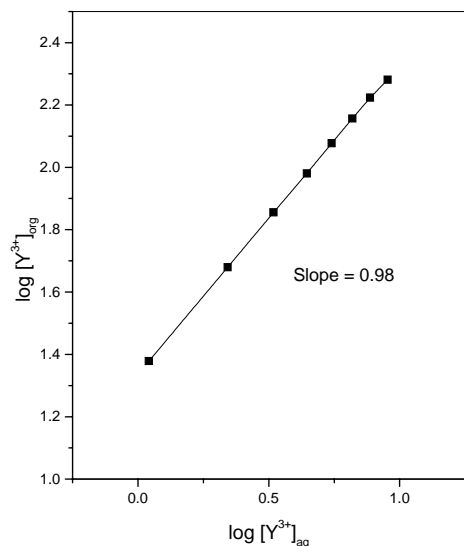
2.00	97.3	81.7	81.1
2.50	97.2	81.7	81.2

### Effect of Metal Ion Concentration

The log-log plot of equilibrium organic phase metal concentration against the aqueous phase metal concentration is given in Fig. (3). This relation gives a straight line in the concentration range 25 – 200 mg/l of Y(III) with slope around 1.0. This indicates that only mononuclear yttrium species seems to be extracted into the organic phase.



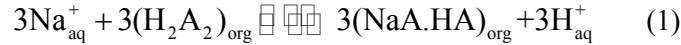
**Fig.(2):** Effect of Ionquest 801 concentration in kerosene on extraction of yttrium (100 mg/l) from 2 M NaCl, at pH 1.7 and  $25 \pm 1$  °C.



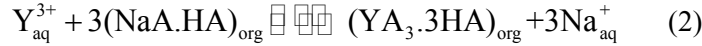
**Fig.(3):** Effect of initial yttrium concentration on its extraction from 2 M NaCl, at pH 1.7 by 0.015 M Ionquest 801 in kerosene at  $25 \pm 1$  °C.

### Extraction Equilibrium

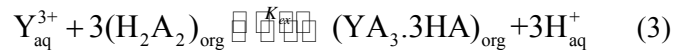
It was reported<sup>(14)</sup> that dialkyl organophosphorus acidic extractants (HA) are present as dimers (H<sub>2</sub>A<sub>2</sub>) in non polar aliphatic solvents. In addition, in case of neutralizing EHEHPA with Na<sup>+</sup> ions, the process can be expressed as:



The equilibration process between Y(III) and the neutralized EHEHPA can be expressed as follows:



where the stoichiometry of the extracted species of yttrium was determined on the basis of conventional slope analysis of the experimental results. Therefore, at equilibrium the overall reaction of the extraction of trivalent yttrium ion, Y<sup>3+</sup>, with a chelating extractant may be represented as:



where K<sub>ex</sub> is the equilibrium constant. As shown from the above equations (1-3), the sodium salt present in aqueous solution has no role in the equilibrium and it acts only as a catalyst which enhances the process (as indicated before).

The equilibrium constant, K<sub>ex</sub> for reaction (3) is expressed as:  $K_{ex} = \frac{[\text{YA}_3.3\text{HA}]_{\text{org}} [\text{H}^{+}]_{\text{aq}}^3}{[\text{Y}^{3+}]_{\text{aq}} [\text{H}_2\text{A}_2]_{\text{org}}^3}$  (4)

The distribution ratio, D, of yttrium, can be written from equation (3) as:

$$D = \frac{[\text{YA}_3.3\text{HA}]_{\text{org}}}{[\text{Y}^{3+}]_{\text{aq}}} \quad (5)$$

by substituting from equation (5) into equation (4):  $K_{ex} = \frac{D[\text{H}^{+}]_{\text{aq}}^3}{[\text{H}_2\text{A}_2]_{\text{org}}^3}$  (6)

Taking the logarithm of both sides of the above equation a linear relation is obtained:

$$\log K_{ex} = \log D + 3 \log [\text{H}^{+}]_{\text{aq}} - 3 \log [\text{H}_2\text{A}_2]_{\text{org}} \quad (7)$$

where, H<sub>2</sub>A<sub>2</sub> is the effective concentration of EHEHPA.

The extraction constant was calculated at pH 1.7 and different concentrations of EHEHPA. The results obtained are given in Table 6. Also, the extraction constant was calculated at constant extractant concentration (0.015 M) and different pHs. The obtained results are listed in Table 7. From these results it is clear that K<sub>ex</sub> values are almost constant with an average value of 409.9 ± 4.33 which justifies the proposed extraction equilibrium of Y(III) by EHEHPA in kerosene, based on the experimental results, under the investigated extraction conditions.

### Effect of Temperature and Thermodynamic Functions

Effect of temperature on the extraction of Y(III) dissolved in 2 M sodium chloride solution of pH 1.7 by 0.015 M EHEHPA in kerosene was studied by varying its temperature in

the range 10-50 °C. The obtained results showed that extraction of yttrium decreased as the temperature increased. The extraction constant ( $K_{ex}$ ) values of the extracted species are evaluated with respect to temperature

**Table 6: Extraction constant ( $K_{ex}$ ) of yttrium (100 mg/l) in chloride medium of pH 1.7 by different concentrations of EHEHPA in kerosene at  $25 \pm 1$  °C.**

<b>[Ionquest 801] M</b>	<b>Distribution ratio (D)</b>	<b>Extraction Constant (<math>K_{ex}</math>)</b>
0.001	0.006	406.70
0.005	0.801	407.20
0.01	6.410	407.33
0.015	21.600	406.70
0.02	51.290	407.41
0.03	173.090	407.38
$K_{ex}$ (average)		$407.19 \pm 0.49$

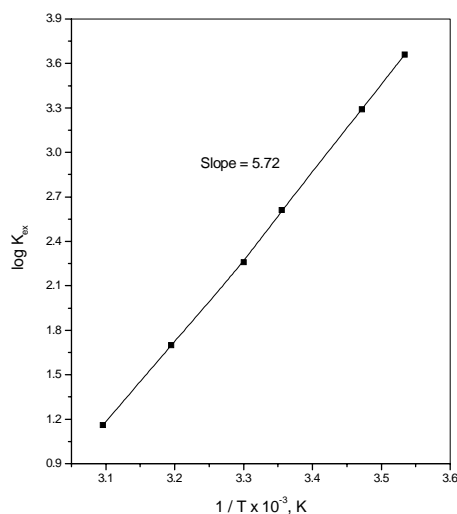
**Table 7: Extraction constant ( $K_{ex}$ ) of yttrium (100 mg/l) in chloride medium by EHEHPA (0.015 M) in kerosene at different pHs and  $25 \pm 1$  °C.**

<b>pH</b>	<b>Distribution ratio (D)</b>	<b>Extraction Constant (<math>K_{ex}</math>)</b>
0.5	0.006	412.27
0.7	0.022	414.23
1.0	0.174	412.44
1.2	0.692	412.02
1.4	2.75	411.29
1.7	21.93	412.91
$K_{ex}$		$412.53 \pm 1.70$



degrees according to equation (7). Plotting the reciprocal of the absolute temperature experimented ( $1/T$ )  $K^{-1}$  versus the respective  $\log K_{ex}$  values yielded a straight line with a positive slope of  $5.72 \times 10^3$ , Fig. (4), which indicates that the extraction is exothermic.

The temperature effect on Y(III) extraction is evaluated in terms of the thermodynamic functions ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) calculated from van't Hoff equations <sup>(14)</sup>, table 8. The negative  $\Delta H$  value (-10.57 kJ/mol) indicates the exothermic character of the extraction process. The positive  $\Delta S$  value (14.50 J/mol K) indicates that the obtained extracted yttrium species is less ordered.



**Fig. (4): Effect of temperature on extraction of yttrium (100 mg/l) from 2 M NaCl, at pH 1.7 by 0.015 M Ionquest 801 in kerosene.**

**Table 8: Thermodynamic functions for yttrium extraction from 2 M NaCl, at pH 1.7 by 0.015 M Ionquest 801 in kerosene.**

Thermodynamic function	Calculated value
Enthalpy change ( $\Delta H$ )	-10.57 kJ/mol
Free energy change ( $\Delta G$ )	-14.89 kJ/mol
Entropy changes ( $\Delta S$ )	14.50 J/mol K

### Effect of Stripping Agent

Back extraction of yttrium from the loaded organic solution was carried out with different stripping agents, Table 9. The stripping was found to be quantitative with 2 M H<sub>2</sub>SO<sub>4</sub> or with 3 M HCl.

Table 9: Stripping of Y(III) from loaded Ionquest 801 in kerosene solution using different reagents at 25 ± 1 °C.

Stripping reagent	Stripper concentration, M	% stripped of Y <sup>3+</sup> in aqueous phase
HNO <sub>3</sub>	0.1	2.5
	0.5	12.7
	1.0	25.4
	2.0	50.9
	3	76.2
HCl	0.1	0.1
	0.5	9.1
	1.0	44.4
	2.0	95.4
	2.5	99.2
	3	~ 100
H <sub>2</sub> SO <sub>4</sub>	0.1	7.2
	0.5	37.2
	1.0	73.6
	2.0	~ 100
Water	--	3.7

### CONCLUSION

From the obtained results it was found that yttrium is extracted from 2M sodium chloride medium with EHEHPA by a cation exchange mechanism. The neutralized form of EHEHPA was observed to be more efficient for extraction of yttrium from chloride medium than the acidic EHEHPA form. The extraction with neutralized extractant was imposed by adding 2 M NaCl solution to the aqueous phase. The dielectric constant of the diluents was found as an important

parameter affecting extraction of Y(III) where as the dielectric constant decreases the extraction increases. The extraction was found to be quantitative using an organic phase of 0.04 M Ionquest 801 and an aqueous phase of pH 1.7. The stoichiometry of the extracted species was determined by conventional slope analysis method and found to be mainly in the form  $YA_3.3HA$ . The extraction process is an exothermic reaction as indicated by the effect of temperature on the extraction process. Quantitative stripping of Y(III) from loaded Ionquest 801 could be done by aqueous solutions of 3 M HCl or 2 M  $H_2SO_4$ .

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