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SYNTHESIS AND CHARACTERIZATION OF N-OCTANOYL-4-METHYLPIPERDINE AS EXTRACTANT FOR Pr(III) IONS FROM SULFURIC ACID SOLUTION

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ABSTRACT

N-octanoyl-4-methylpiperdine (NOMP), has been synthesized (as a novel extractant), before being characterized by elemental analysis, FTIR spectroscopy, mass spectrometry, ^{1}H, and ^{13}C-NMR. Praseodymium [Pr(III)] extraction from sulfate medium has been investigated in batch systems. The effects of different experimental parameters such as extractant concentration, initial solution pH, diluents, equilibration time and temperature on extraction performance and principal factors affecting the stripping efficiency have been determined. Quantitative Pr(III) extraction was achieved in 5 min with 0.08 M NOMP in kerosene in four stages at aqueous: organic (A:O) phase ratio of 1:1 at equilibrium pH 1.6. The thermodynamic study shows that the reaction is spontaneous, and exothermic. Nitric acid solutions (4 mol/L) can be efficiently used for metal recovery and NOMP extractant can be recycled for at least 5 cycles with limited decrease in extraction efficiency. Finally, an application of the proposed method Pr_2O_3 94.35 % is obtained from a rare earth concentrate of 5.38% Pr_2O_3 prepared industrially from Egyptian chemical processing plant of monazite sand of the Nuclear Materials Authority.

INTRODUCTION

Rare earth elements are strategic resources widely used in advanced technologies such as; electronic and communication devices, high-performance alloys, magnets, glasses, ceramics and catalysts. The balance request/production became a geopolitical and economic stake. For these reasons there are incentive politics for developing methods and processes for a better recycling of these strategic elements from spent materials and equipment and for valorizing low-concentration mineral resources Xie et al. (2014), Galhoum et al. (2017), Wikipedia (2019), Yoon et al. (2015), Wilson et al. (2014), Rabatho et al. (2013). Rare earth elements have unique physicco-chemical properties that make them essential elements in many high-tech components. Bastnesite (La, Ce)FCO_3, monazite, (Ce, La, Y, Th)PO_4, and xenotime, YPO_4, are the main commercial sources of rare earths Xie et al. (2014).

Praseodymium (Pr) always occurs naturally together with the other rare-earth metals. It is the fourth most common rare-earth element, making up 9.1 parts per million of the Earth's crust, an abundance similar to that of boron Wikipedia (2019). Different rare earths are needed to supply the required functionality in these applications. In some cases, a single rare earth element may be required, such as Pr is used in high-intensity permanent magnets,

which are essential in electric motors and generators used in hybrid cars and wind turbines also, for nickel metal hydride rechargeable batteries. The metal is used as an alloying agent with magnesium creating a high-strength metal for aircraft engines. It is also used to make specialized yellow glass goggles for glass blowers and blenders. Flame lighter flints use misch metal (a rare earth alloy) containing Pr to produce sparks by friction. Pr salts are used to color glasses and enamels Xie et al. (2014), Singh and Gupta (2000).

Metal recovery from their sources is frequently applying hydrometallurgical processes Yoon et al. (2015), Wilson et al. (2014), Rabatho et al. (2013), Singh and Gupta (2000): (a) first leaching using in most cases acidic solutions Yoon et al. (2015), followed by (b) a series of separation techniques including precipitation Rabatho et al. (2013), solvent extraction Wilson et al. (2014), ion-exchange or chelating resins Galhoum et al. (2017). In hydrometallurgical process, to recover metals from minerals or from secondary sources the key operations is leaching Yoon et al. (2015), Wilson et al. (2014). Rare earth minerals are usually leached with aqueous inorganic acids, such as HCl, H_2SO_4, or HNO_3. After filtration, solvent extraction is usually used to separate individual rare earths or produce mixed rare earth solutions or compounds. Rare earth producers follow similar principles and schemes when selecting specific solvent extraction routes Xie et al. (2014), Yoon et al. (2015). Solvent extraction has the advantages of being easily engineered for continuous operations and has proved remarkably robust since its introduction for uranium production Rabatho et al. (2013). The choice of extractants and aqueous solutions is influenced by both cost considerations and requirements of technical performance Wilson et al. (2014), Singh and Gupta (2000).

Commercially; D2EHPA, HEHEHP, Versatic 10, TBP, and Aliquat 336 have been widely used in rare earth solvent extraction processes. Up to hundreds of stages of mixers and settlers may be assembled together to achieve the necessary separations Galhoum et al. (2017), Wilson et al. (2014), Miller (2000).

In recent years, amides have been proposed as alternatives for phosphorous-containing compounds as extractants in the nuclear fuel reprocessing because of several advantages, such as complete incinerability, high chemical and radiolytic stability, simplicity of synthesis and easy removal of the degradation products Pathak et al. (2001), Mowafy and Aly (2001), Chan et al. (1997). The structures of extractants have been a major concern in the development of new extractants with a potential high extracting power for metal ions. Yuan (1980), Xu and Yuan (1987) pointed out that electron density at the active site, steric effects and lipophilicity of an extractant are the main factors affecting the extracting power for metal ions. Since Siddall III first studied *N,N'*-dialkylamides as extractants for the separation of actinides in 1960 Siddall III (1960), they were regarded as alternatives to TBP in the reprocessing of nuclear fuel. During the last forty years, many publications have described the remarkable properties of *N,N'*-dialkylamides in the field of solvent extraction Guo-Xin (1998). It has been shown that they are potentially good extractants for actinides, especially for U(VI) Guo-Xin (1998). However, there are no additional studies of extraction of rare earth elements using N-octanoyl-4-methylpiperdine (NOMP).

In the present study, synthesis of N-octanoyl-4-methylpiperdine (NOMP) as extractant for Pr(III) ions. The extractant was characterized by elemental analysis, FTIR spectroscopy, mass spectrometry, ^{1}H, and ^{13}C-NMR. In a second step the preliminary laboratory investigation, emphasis on the extraction of Pr(III) from sulfuric acid solutions this carried out to get a better understanding of the extraction behavior of individual elements as part of an overall study on the separation of Pr(III) from rare earth concentrate obtained from alkaline leaching of Egyptian monazite.

EXPERIMENTAL

Reagents and Analysis

4-Methylpiperdine, octanoic acid, thionyl chloride (SOCl$_2$) supplied by Fluka. Odorless kerosene (non-aromatic) was obtained from Misr Petroleum Company, Egypt. Stock solution of Pr(III) ion was prepared from Pr$_2$O$_3$ supplied by Fluka in concentrated sulfuric acid and diluted with distilled water to a final concentration of 1000 mg L^{-1}. Arsenazo III (A.R grade) was obtained from Fluka and all other chemicals were Prolabo products and were used as received. The other lanthanides concentration was determined by Atomic Absorption Spectroscopy (AAS) PERKIN-ELMER AAnalyst100. All measurements were carried out at laboratory temperature.

Synthesis of N-octanoyl-4-methylpiperdine

The N-octanoyl-4-methylpiperdine (NOMP) was synthesis in two steps, as shown in Scheme (1). The piperdine based amides, was prepared according to a modified literature procedure Xing-Cun et al. (2003). The relevant acid chloride was first prepared by reaction of octanoic acid (5.09g, 0.0348 mol) was added to thionyl chloride (20 ml) and heated under reflux for 5 hrs. The excess thionyl chloride was removed under reduced pressure to yield a yellow liquid which was used without further purification, and then reacted with 4-methylpiperidine (10 g, 0.100827 mol) in chloroform (50 ml) was added to a solution of potassium carbonate (10 g) in distilled water (50 ml) and the mixture stirred at room temperature for 3 hrs. Octanoyl chloride (5.7g mol) added to the reaction mixture and stirred for 2 hrs. The reaction mixture was cooled, the organic layer separated, dried over magnesium sulfate and the solvent evaporated *in vacuo* to yield a yellow oil. This ligand has been observed as an extractant subduing the above-mentioned shortcomings of other extractants. It has low aqueous solubility, complete miscibility with all the commonly employed organic diluents and is reasonably resistant to hydrolysis. Also the new extractant is free of any objectionable odor and offers a quicker phase separation.

Characterization of Material

Microanalyses were obtained at the University of Leeds Microanalytical Service. NMR spectra of N-octanoyl-4-methylpiperdine were recorded by the author using either a Bruker ARX 250 spectrometer or a Bruker DPX 300 spectrometer. The elemental analysis was characterized using an automatic analyzer (CHNS Vario EL IIIelementar analyzer, Elementar, Germany).
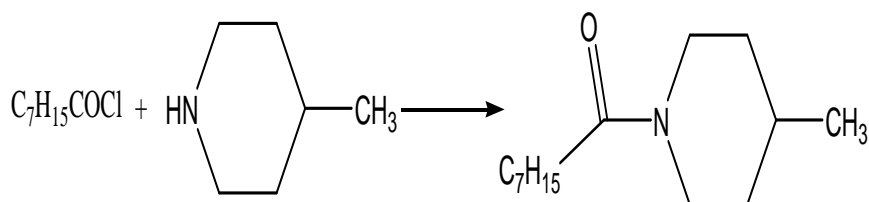
Extraction Procedure

Batch experiments were carried out by equilibrating equal volumes of aqueous phase 10 ml and organic phase for 10 minutes under mixing in a magnetic stirring. After phase separation, known aliquots of the aqueous phase were sampled for analysis. The distribution ratio (D) was measured as the ratio between the concentration of Pr(III) ions in the organic phase to the aqueous phase. All experiments were carried out by equilibrating for 5 min at room temperature (25 ±1 °C) and pH 1.6; except when the effect of time, pH and temperature on the distribution equilibria was studied. For the back-extraction studies the organic phase was loaded with a certain amounts of Pr(III). A certain volume of the loaded organic solution was mixed with equal volume of aqueous solution containing the strippant using magnetic shaker for 5 min.

RESULTS AND DISCUSSION

Synthesis and Characterization of Extractant

Scheme (1) shows the general procedure for the synthesis of N-octanoyl-4-methylpiperdine and the tentative chemical structure of the extractant. Table 1. Results N-octanoyl-4-methylpiperdine analysis (NOMP). The ligand was characterized by ^{1}H and ^{13}C-NMR (Fig 1&2), mass spectrometry and elemental analysis, and yield: 12.55g, (0.056 mol, 79.94 %).

$$C_7H_{15}COOH + SOCl_2 \cdot \quad C_7H_{15}COCl + SO_2 + HCl$$

$$C_7H_{15}COCl + HN\underset{}{\overset{}{\bigcirc}}-CH_3 \longrightarrow \underset{C_7H_{15}}{\overset{O}{\parallel}}C-N\underset{}{\overset{}{\bigcirc}}-CH_3$$

Scheme 1: Synthesis of N-octanoyl-4-methylpiperidine

Table 1: Results of N-octanoyl-4-methylpiperdine analysis

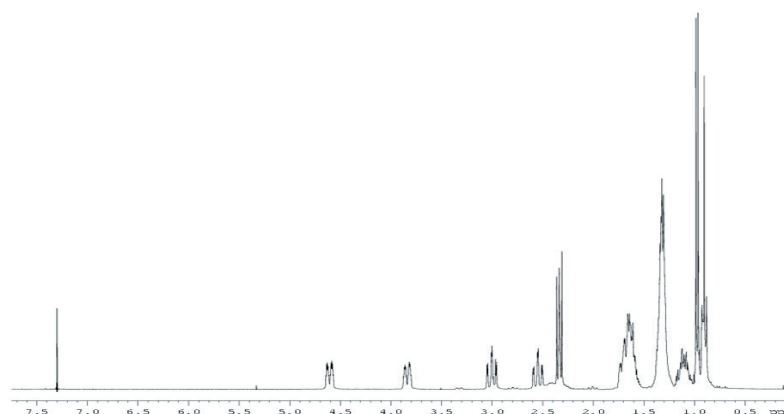| Sample	N-octanoyl-4-methylpiperdine
IR ($V_{C=O}$), cm^{-1}	1646.3
^{1}H NMR (300.13 MHz, CDCl$_3$, 298 K).	A- 4.64-4.57 (m, 1H, $\underline{H}$C-N of C$_5$N ring), 3.88-3.80 (m, 1H, $\underline{H}$C-N of C$_5$N ring), 3.00 (pseudo t of d, 1H, J_1= 12.60 Hz, J_2 = 2.50 Hz, $\underline{H}$C-N of C$_5$N ring), 2.54 (pseudo t of d, 1H, J_1 = 12.80 Hz, J_2=2.50 Hz, $\underline{H}$C-N of C$_5$N ring), 2.33 (t, 2H, ^3J = 7.6 Hz, C$\underline{H}_2$ of C$_6$H$_{13}$-CH$_2$C=O), 1.73-1.55 (m, 5H, aliphatic C$\underline{H}$), 1.37-1.23 (m, 8H, aliphatic C$\underline{H}$), 1.18-1.02 (m, 2H, aliphatic C$\underline{H}$), 1.00-0.94 (m, 3H, C$\underline{H}_3$) and 0.92-0.88 (m, 3H, C$\underline{H}_3$).
^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$, 298 K).	B-169.91 (C=O), 44.37, 40.32 ($\underline{C}$N of C$_5$N), 33.12, 32.19, 31.91, 30.08, 29.50, 27.87, 27.47, 32.88, 20.98, 20.12 (aliphatic $\underline{C}$) and 12.45 (CH$_3$ of C$_7$H$_{15}$)
Elemental analysis, %	Calculated: C: 74.61; H: 12.07; N:6 .21 Found: C: 73.7; H: 12.85; N: 7.2
MS (ES$^+$)	225.80 [M$^+$]

Fig. 1: ^{1}H NMR [CDCl$_3$] spectrum of N-octanoyl-4-methylpiperdine (300 K)
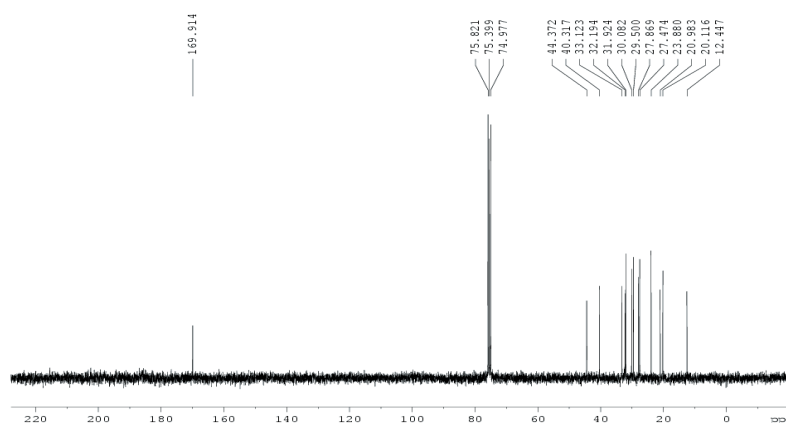

Fig. 2: ^{13}C- NMR [CDCl$_3$] spectrum of N-octanoyl-4-methylpiperdine (300K)

Effect of Different Concentrations of NOMP

The effect of extractant concentrations on the extraction efficiency of Pr(III) was studied in the range 0.01–0.10 M ligand. The distribution ratio of Pr(III) increased steadily from 2.12 to 8.79 with an increase of NOMP concentration from 0.01M to 0.08M in CCl$_4$, and then plateaue. A plot of log D versus log [NOMP] is presented on Figure (3), which shows a linear correlation with a slope ~2 indicating the requirement of two moles of NOMP for each mole of the Pr(III) Desouky et al. (2009).

Effect of Equilibration Time

The effect of equilibrium time (1.0 – 40 min) on the extraction of Pr(III) was studied using 0.08M NOMP in CCl$_4$ while other factors were kept constant. The results (±0.5%) shown on Figure (4) clearly indicate that the
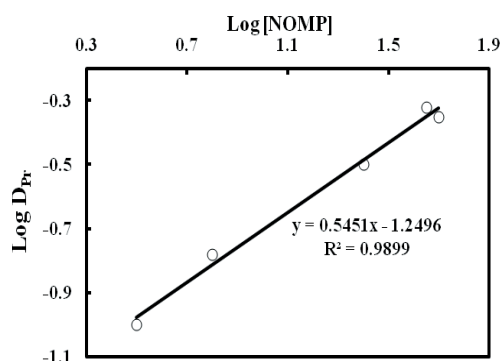
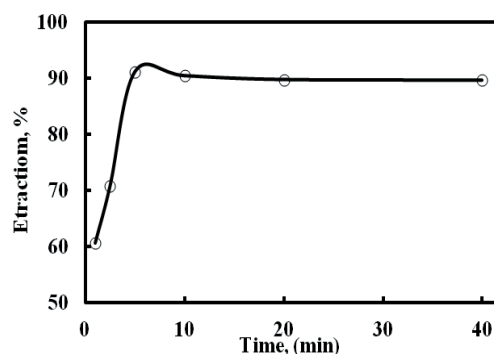Fig. 3: Plot of log D versus log[NOMP] pH=1.5,CCl_4 as diluent

Fig. 4: Effect of contact time on the Pr(III) extraction percent

extraction is fast and 5 min is quite adequate for efficient Pr(III) distribution ratio and by increasing the shaking time the distribution ratio is slightly decreased, and this behavior probably due to the entrainment of some organic phase droplets into aqueous phase, which causes decrease in the extractive power of extractant.

Effect of pH

The distribution ratio of Pr(III) from aqueous sulfate medium was studied using 0.08M NOMP in CCl_4 within the initial pH range 0.4–2.1. As shown on Figure (5), the dis-

tribution coefficient of Pr(III) reached a maximum at equilibrium pH 1.6 where the formation of an ion-pair complex in sulfate media is favorable this results finds agree with our previous work on yttrium Desouky et al. (2009). With a further increase in pH to 2.1, Pr(III) distribution coefficient decreased; may be result from the formation of non-extractable praseodymium species as a result of complication with components of aqueous phase. This occurs, in sulfate media due to equilibria between SO_4^{2-}, HSO_4^-, and H_2SO_4 resulting in the formation of Pr complexes with these anions. At higher pH, there is a possibility of hydrolysis of the Pr(III) ion-pair complex. This indirectly promotes competing equilibria with the formation of ion-pair complex, resulting in a decrease in extractability with an increase in pH Desouky et al. (2009), El-Yamani and Shabana (1985).

Effect of Diluents

The Pr(III) distribution ratio has been studied using different organic aromatic and aliphatic diluents were tested namely chloroform, carbon tetrachloride, toluene, benzene, o-xylene, and kerosene as diluents for the distribution ratio of Pr(III) with 0.08 M NOMP (Table 2). The distribution coefficient of Pr(III) was maximum with kerosene, chloroform and carbon tetrachloride as diluents but benzene, p-xylene and toluene proved to be
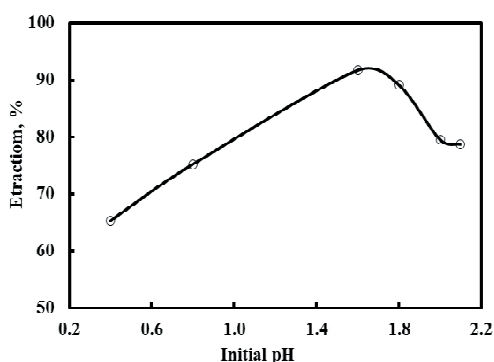

Fig. 5: Effect of initial pH on the Pr(III) extraction perecnt

Table 2: Extraction of Pr(III) by N-octanoyl-4-methylpiperdine as a function of diluents

Diluents	Dielectric constant	Distribution coefficient	Extraction, [%]
Benzene	2.30	7.45	87.57
Toluene	2.23	7.21	87.13
O-xylene	2.28	6.51	86.93
Chloroform	5.10	8.83	89.82
Carbon tetrachloride	2.23	9.50	91.00
Kerosene	2.00	11.94	92.62

(0.08M N-octanoyl-4-methylpiperdine; Aq:Org (1:1); time 5 min; room temp.)

poor diluents. It is reported that there is sometimes a correlation between the effect of a diluent and its dielectric constant but no such correlation was found in our present study. Results are presented in Table (2). Short equilibrium time and good phase separation was achieved when aliphatic diluents were used compared to aromatic diluents. Considering several factors like cost, environmental and safety aspects and maximum Pr(III) distribution coefficient, kerosene was preferred as the diluent for further Pr(III) extraction studies Desouky et al. (2009).

Effect of Aqueous: Organic Phase Ratio

The aqueous: organic phase ratio has a significant effect on the distribution ratio and entrainment. This effect was investigated by changing the aqueous: organic phase ratio from 1:1 to 1:4 at concentration 0.08M ligand dissolved in kerosene. The results presented in Table (3) it is obvious that a phase ratio of 1:1 gives the best Pr(III) extraction. At this phase ratio the rate of coalescence and re-dispersion of the dispersed phase is also enhanced.

Effect of Temperature

The extraction of a metal complex into an organic phase involves large changes in enthalpy (solvation processes) and in entropy (solvent orientation and restructuring), leading to considerable temperature effects Desouky et al. (2009). To study the effect of tempera-

Table 3: Effect of Aq.: Org. phase ratio on the extraction process

Phase ratio, (Aq.:Org.)	Distribution coefficient	Extraction (%)
1:1	12.24	93.12
1:2	8.91	85.01
1:3	6.33	71.23
1:4	2.56	65.13

ture on Pr(III) distribution coefficient, experiments were carried in the range 298–333K.

The results obtained showed that the Pr(III) distribution ratio decreased. This behavior is agrees with that reported by previous investigators Pathak et al. (2001), Desouky et al. (2009). Figure (6) plots Log D versus $1000/T$, K^{-1} which gives a straight line for the extraction of Pr(III) by NOMP from 0.3 M H_2SO_4 solution. The ΔH value for Pr(III) was -31 kJ/mol - as calculated from the slope using the Van't Hoff equation (Eq. (1)).
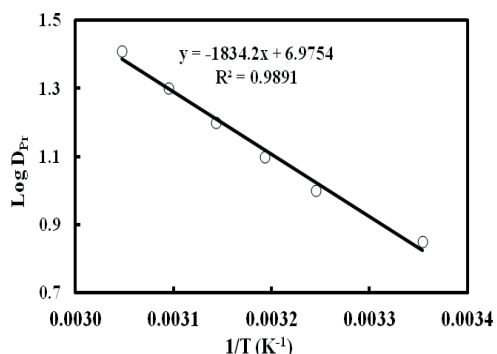
$$Log\ D = -\Delta H/2.303RT + C \qquad (Eq.\ 1)$$

Fig. 6 : Plot of D_{Pr} against 1/T, K^{-1} for extraction of Pr(III)

where D is the distribution ratio, ΔH the enthalpy change for the extraction reaction, R is the universal gas constant (8.314 J/mol k) and C is a constant for the system. This value of ΔH was used to obtain the corresponding free energy ($\Delta G = -7.2$ kJ/mol) and entropy ($\Delta S = 53$ J/mol K) at 298 K using Eqs. (2) and (3), respectively:

$$\Delta G = -2.303RT \log D \qquad (2)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

The negative value of ΔH indicates that the extraction of Pr(III) in this system is an exothermic process and the reaction becomes more favourable at room temperatures.

Extraction Isotherm

The number of the theoretical stages was calculated by the McCabe-Thiele diagram which was constructed by standard procedure and is given on Figure (7). Equal volumes of the organic phase (0.08M NOMP in kerosene) and aqueous phase were contacted for five minutes until equilibrium was obtained the phases were allowed to separate and the aqueous phase was removed and analyzed. Fresh aqueous solution was added to the organic phase to give the same phase ratio as that originally used and the procedure repeated. Care must be taken to keep the same pH value throughout the series of shake-outs. In constructing this diagram, the data was used

to obtain extraction isotherm curve by plotting Pr(III) concentration in the organic phase against its concentration in the aqueous phase. A vertical line is then drawn from the concentration of Pr(III) in the feed solution on the x-axis. The operating line is next inserted, the slope of which is equal to the phase ratio. From Figure (7), we can see Pr(III) extraction under these conditions needs four extraction stages for nearly complete recovery.

Pr(III) Stripping and Recycling Studies

Stripping is the reverse of the extraction, so it should be promoted by these factors that affect extraction negatively. Pr(III) stripping from loaded organic solvent, were investigated using various stripping agents, such as HCl, H_2SO_4 and HNO_3, in the range 0.5–6 mol/L and O:A ratio of 1:1. The results are presented in Table (4). From the results, it is clear that 4 mol/L HNO_3 is the most effective acid for the quantitative stripping of Pr(III). Variation of the stripping period showed that 5 minutes equilibration time were sufficient for quantitative recovery of Pr(III) from organic phase. Pr(III) ions can be stripped from Pr-loaded NOMP solution into 4 mol/L HNO_3, where 10 % oxalic acid was added gradually to the obtained strip liquor rich in Pr(III), and was left for 24 hours where praseodymium oxalates ($Pr_2(C_2O_4)_3 \cdot xH_2O$) were obtained.
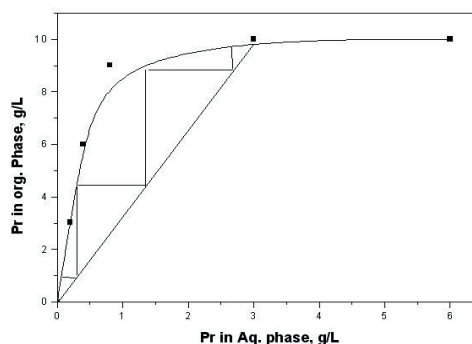

Fig. 7: McCabe-Thiele diagram for Pr(III) extraction

Table 4: Effect of stripping agents on stripping efficiency

Acid conc., (mol/L)	Stripping efficiency, [%]		
	H_2SO_4	HNO_3	HCl
0.3	40	43	37
0.6	47	53	43
1	62	66	55
4	84	88	73
6	62	72	58

Table 5: Effect of successive extraction cycles on the solvent regeneration efficiency, [%]

Cycle number	1st	2nd	3rd	4th	5th	6th
RE [%]	91.31	91.08	89.52	89.05	86.87	83.72

Stability and Regeneration Capacity of NOMP

Experiments were conducted to check the chemical stability of 0.08M ligand dissolved in kerosene towards long-term mixing with 0.3M H_2SO_4. The extraction of Pr(III) was periodically tested after 3 days. A negligible variation nearly 1% in the distribution coefficient and percent extraction of Pr(III) ion was observed even after a contact of the extractant with the acid for 40 days.

NATURAL ORE APPLICATION

The starting material for the rare earth cake is a concentrate of monazite sands with nearly 97% purity. This concentrate is obtained from black sand, upgraded by physical dressing techniques at the Nuclear Materials Authority. In the application studies, the Pr(III) extraction from rare earth hydrous oxide concentrate, which reacted with sulfuric acid according to the following overall reactions:

$$RE_2O_3 + 3H_2SO_4 \rightarrow RE_2(SO_4)_3 + 3H_2O \quad (5)$$

$$2RE(OH)_3 + 3H_2SO_4 \rightarrow RE_2(SO_4)_3 + 6H_2O \quad (6)$$
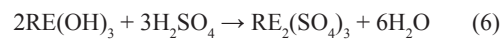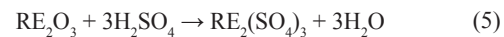
Rare earth concentrate (5 g) was heated with 1L 0.3M sulfuric acid at $\approx 80^oC$ for two hour to allow complete dissolution of all rare earth elements, and then filtrated. The filtrate contained most rare earth elements. Chemical analysis of rare earth concentrate was estimated by energy dispersive analysis with X-rays (EDAX). For this work a REE concentrate containing (%) Nd_2O_3 16.91, La_2O_3

From economical point of view, regeneration and reuse of organic solvent is important for industrial application. After Pr(III) separation, still some of the Pr(III) remained in the organic phase. The Pr(III) containing organic phases were stripped with 4 mol/L nitric acid at an equal phase ratio. The stripped organic phases were again washed with distilled water for 2 to 3 times. The regenerated stripped solvents were reused for the extraction of Pr(III). The process was repeated for five cycles, and the solvent regeneration efficiency (RE, %) was calculated from Eq. (4), the results revealed that a practically insignificant (standard deviation of ±1.5%) change in the efficiency of the reagents, suggesting that the extractant is stable under the present experimental conditions. As shown in Table 5, nearly no appropriate changes over five cycles during successive extraction cycles. This indicates that the NOMP can be regenerated and reused after many cycles by nearly same efficient without any degradation products.

$$RE, \% = \frac{Amount\ extracted\ in\ 2^{nd}\ cycle}{Amount\ extracted\ in\ 1^{st}\ cycle} \times 100 \quad (4)$$

12.42, Y_2O_3 2.16, Gd_2O_3 1.89, Eu_2O_3 1.71, Sm_2O_3 2.81, Pr_2O_3 5.38, Ce_2O_3 31.29, and Na_2O 24.81 is used. The mentioned concentrate was produced industrially from the chemical treatment of monazite sand by Nuclear Materials Authority in Egypt. According to the high percent of Ce_2O_3 31.29 % which affect the liquid-liquid extraction of Pr, Ce should be first removed following the procedure given by Morais et al. (2003).

Solvent Extraction of Praseodymium Rich Fraction

The obtained mother liquid solution is evaporated to such a consistency that it would solidify upon cooling. When it has cooled down considerably, but while still liquid, the mother liquor is poured off and the crystals well drained. The mother liquid is then poured off and evaporated further; the liquid and crystals are systematically fractionated by continuing the evaporating as described above for 2hr. The solution must be allowed to become alkaline gradually by boiling too long. The almost quantity of lanthanum separates in the first fraction, together with trace amount of non-separated Ce(IV). The second fraction contains Pr and Nd(III) which are precipitated with trace amount of Sm(III) and Gd(III) where Pr(III) and Nd(III) occur together, fractions of the same colour are united. After removal of cerium the mother liquid solution is evaporated and cooled many times to obtain fraction (II) which is rich in praseodymium starting from 5.38 % Pr_2O_3 and up to 16.91 % Pr_2O_3. Separation of Pr(III), the best source for praseodymium is found in fraction (II). The above fraction rich in praseodymium is dissolved in 0.3M sulfuric acid. Solvent extraction of Pr(III) from sulfate liquor was carried out in four stages with a 0.08M N-octanoyl-4-methylpiperdine in kerosene at the obtained bench scale results, followed by stripping in two stages with 4M nitric acid at an organic: aqueous phase ratio of 1:1. Recovery of the strip liquors was 92–93% for Pr. Praseodymium was precipitated as praseodymium oxalate ($Pr_2(C_2O_4)_3$:xH_2O) and ignit-ed to Pr_2O_3. The final product is a 94.35 % Pr_2O_3 together with smaller amounts of 2.5% Nd_2O_3, 1.94% Gd_2O_3, and 1.01% Sm_2O_3.

CONCLUSIONS

Solvent extraction studies of Pr(III) from sulfuric acid solutions by NOMP which can be easily synthesized and showed that this extractant is a promising one in the separation and purification of praseodymium from rare earth concentrate as summarized in the following points:

1. N-octanoyl-4-methylpiperdine (NOMP), has been synthesized (as a novel extractant) for Pr(III) ions from sulfuric acid solution.

2. NOMP extractant was characterized by elemental analysis, mass spectrometry, ^{1}H, and ^{13}C-NMR.

3. Pr(III) extraction efficiency was achieved with 0.08M NOMP in kerosene, at an organic: aqueous (O/A) phase ratio of 1:1, equilibrium pH of 1.6 and for 5 minutes contact time.

4. Kerosene is showed good as diluent for NOMP comparing with the other diluents used.

5. Pr(III) stripping is achieved using 4 mol/L HNO_3 at an O:A ratio of 1:1 and 5 minutes contact time is recommended for quantitative stripping efficiency.

6. As an application of the proposed method, a final Pr_2O_3 of ca. 94.35% is obtained from a praseodymium rich rare earth concentrate of 16.91% Pr_2O_3 produced industrially from the chemical processing plant of monazite at the Nuclear Materials Authority, Egypt.

REFERENCES

Chan, G.Y.S.; Drew, M.G.B.; Hudson, M.J.; Iveson, P.B.; Liljenzin, J.O.; Skalberg, M.; Spjuth, L., and Madic, C., 1997. Separation of americium (III) from europium (III) with tridentate heterocyclic nitrogen ligands and crystallographic

studies of complexes formed by 2,2′:6′,2″-ter-pyridine with the lanthanides. J. Chem. Soc., Dalton Trans., 821-830.

Desouky, O.A.; Daher, A.M.; Abdel-Monem, Y.K., and Galhoum, A.A., 2009. Liquid–liquid extraction of yttrium using primene-JMT from acidic sulfate solutions. Hydrometallurgy, 96, 313-317.

El-Yamani, I.S., and Shabana. E.I., 1985. Solvent extraction of lanthanium (III) from sulfuric acid solutions by primene -JMT. J. Less-Common Met., 105, 255-261.

Galhoum, A.A.; Hassan, K.M.; Desouky, O.A.; Masoud, A.M.; Akashi, T.; Sakai, Y.E., and Guibal, E., 2017. Aspartic acid grafting on cellulose and chitosan for enhanced Nd (III) sorption. Reactive and Functional Polymers, 113, 13-22.

Guo-Xin, S., 1998. Physical chemistry of extraction System of U (VI) and Th (IV) with Amide extractans, Ph.D. Thesis, Shanghai Institute of Nuclear research, The Chinese Academy of Sciences.

Miller, H.A.; Lating, N.; Parson, S.; Parkin, A.; Tasker, P.A., and white, D.J., 2000. Supramolecular assemblies from ditopic ligands and transition metal salts. J. Chem. Soc., Dalton Trans., 3773-3782.

Morais, C.A.; Benedetto, J.S., and Ciminelli, V.S.T., 2003. Proc. 5th Inter. Symposium Honoring Professor In: M. Ritchie (ed.), Hydrometallurgy,Vancouver, 2,TMS, 1773-1782.

Mowafy, E.A., and Aly, H.F., 2001. Synthesis and characterization of N, N, N', N'-tetrabutyl-succinamide as extractant for uranium (VI) and thorium (IV) ions from nitric acid solution. J. Radioanal. Nucl. Chem., 250, 199-203.

Pathak, P.N.; Kumbhare, L.B., and Manchanda, V.K., 2001. Uranyl (VI) carbonate complex formation: Validation of the $Ca_2UO_2(CO_3)_3$(aq.) species. Radiochim. Acta, 89, 447p.

Rabatho, J.P.; Tongamp, W.; Takasaki, Y.; Haga, K., and Shibayama, A., 2013. Recovery of Nd and Dy from rare earth magnetic waste sludge by hydrometallurgical process, J. Mater. Cycles Waste Manage. 15, 171–178.

Siddall III, T.H., 1960. J. Phys. Chem., 64, 1683.

Singh, H., and Gupta, C.K., 2000. Mineral Solvent Extraction in Production and Processing of Uranium and Thorium. Process. Extr. Metall. Rev., 21, 307.

Wilson, A.M.; Bailey, P.J.; Tasker, P.A.; Turkington, J.R.; Grant, R.A., and Love, J.B., 2014. Solvent extraction: The coordination chemistry behind extractive metallurgy. Chem. Soc. Rev., 43, 123-134.

Xie, F.; Zhang, T.A.; Dreisinger, D., and Doyle, F., 2014. A critical review on solvent extraction of rare earths from aqueous solutions. Minerals Engineering, 56, 10–28.

Xing-Cun, Y.; Bo-Rong, B.; Guo-Xin, S., and Wei-Guo, C., 2003. N, N'-Dioctanoyl piperazine as a novel extractant for U (VI). J. Radioanal. Nucl. Chem., 258, 677.

Xu, G.X., and Yuan, C.Y., 1987. Solvent Extraction of Rare Earths, Science Publishing House, Beijing, China, 353 (in Chinese).

Yoon, H.S.; Kim, C.J.; Chung, K.W.; Kim, S.D., and Kumar, J.R., 2015. Recovery process development for the rare earths from permanent magnet scraps leach liquors, J. Braz. Chem. Soc., 26, 1143–1151.

Yuan, C.Y., 1980. Proc. Inter. Solvent Extraction Conference, Liege, Belgium, 1, 80.

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تخليق و توصيف ن-اوكتانويل-4- ميثيل بيبردين كمستخلص عضوي لايونات البرازيودميوم من محلول حمض الكبريتيك

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ن-اوكتانويل-٤- ميثيل بيبردين تم تخليقه (مستخلص جديد) و توصيفه و قد تم اثبات التركيب الكيميائى باستخدام تقنيات التحليل العنصرى, طيف الاشعة تحت الحمراء, الطيف الكتلى, (هيدروجين,كربون١٣) الرنين المغناطيسى النووى. لقد تم استخلاص عنصر البرازيودميوم الثلاثى من محلول الكبريتات على نطاق معملى ووجد انه بدراسة بعض العوامل التجريبية مثل تركيز المستخلص,الاس الهيدروجينى, المذيب, زمن الخلط وكذلك درجة الحرارة على عملية الاستخلاص ايضا العوامل الرئيسية المؤثرة على عملية اعادة الاستخلاص تم تقديرها. استخلاص عنصر البرازيودميوم تم بعد زمن خلط 5 دقائق و تركيز ٠,١ مولر للمستخلص المذاب فى الكيروسين على اربعة مراحل و نسبة المائي الى العضوى كانت ١:١ عند اس هيدروجينى ١,٦ و بدراسة الديناميكا الحرارية تبين ان عملية الاستخلاص عملية تلقائية و التفاعل طارد للحرارة, وكان تركيز ٤ مولر حمض النيتريك انسب تركيز لاسترجاع عنصر البرازيودميوم و قد تم التاكد من كفاءة المستخلص باعادة استخدام المستخلص على 5 دورات و كان التاثير محدود.

وفى النهاية تم اجراء تطبيق عملية الاستخلاص على عينة من ركاز العناصر الارضية النادرة المحضرة من وحدة المونازيت بهيئة المواد النووية وكان تركيز اكسيد البرازيودميوم ٥,٣٨٪ فى ركاز العناصر الارضية النادرة الذى وصل بعد عملية الاستخلاص الى ٩٤,٣٥٪ درجة نقاوة.