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Separation of middle rare earths by solvent extraction using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as an extractant

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Abstract: The extraction of the trivalent middle rare earths from chloride media by kerosene solutions of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as an extractant was studied. The separation factors between the elements using solution simulating wastes from NiMH spent batteries have been evaluated: the order of the extractive ability of extractant can be confirmed in $Tb > Gd > Eu > Sm$.

Keywords: solvent extraction; rare earths; separation

Rare earths (RE) elements are a group of 15 elements (atomic numbers 57-71) having their strikingly similar chemical properties and they are conventionally divided into 3 groups: the light (La, Ce, Pr, Nd), middle (Sm, Eu, Gd, Tb) and heavy (Dy to Lu).

The RE elements occur together in nature in some minerals like bastnasite, monazite, xenotime and others; these metal ions have been used for additives to steels or alloys, permanent magnets, hydrogen storage materials, magneto-optic storage discs, electro or cathode ray luminescence, household batteries, etc.^[1,2], therefore in addition to the primary sources such as the commercial-enriched ores of the above referred minerals, wastes such as spent catalysts, super-alloy scrap, spent batteries, sludge, dusts, etc. are potential secondary sources of rare earths.

Some authors^[3] obtained a mixed rare earth oxide product from NiMH spent batteries containing lanthanum, cerium and middle rare earths or developed a hydrometallurgical process^[4] to obtain a precipitate of mixed rare earth from the same type of waste producing an enriched material. The current paper extended the work to establish the laboratory conditions for middle rare earths separation by solvent extraction and to develop a suitable economically viable separation technique for this separation because their value depends on effective separation into high purity compounds.

Several liquid ion exchangers have been used in order to extract metallic species and the most widely used are the phosphoric acid based alkyl phosphorus reagents such as the bis(2-ethylhexyl) phosphoric acid, the 2-ethylhexyl

2-ethylhexylphosphonic acid (EHEHPA) (also known as 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)) and the bis(2-ethylhexyl)phosphinic acid which are applied in the separation and purification of metal cations of different valence^[5,6].

Out of the three types of extractants, the bis(2-ethylhexyl) phosphoric acid is the least selective and the bis(2-ethylhexyl)phosphinic acid, though most selective, is the most expensive. As HEHEPA has been shown to overcome such problems as high acidity required in extraction and stripping and emulsion formation^[7], it may be the best choice.

Some authors investigated the separation of middle RE by combination of electrochemical reduction and solvent extraction^[8-13].

The studies involving middle RE extraction from hydrochloric acid media using HEHEPA are a few and usually carried out at low RE concentrations ($\mu\text{g/L}$ to mg/L), thus further investigation concerning the behaviour of this extraction systems over a relatively wide concentration range seems to be appropriate.

1 Experimental

All reagents were of analytical grade and were used without further purification; in particular the HEHEPA (supplied by Rhodia) was used as received.

As small amounts of diacid such as 2-ethylhexyl phosphonic acid are usually present in this commercial extractant, HEHEPA was titrated by a standardised solution of potas-

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sium hydroxide in a 70 vol.% aqueous solution of acetone. The results of the titration gave a HEHEPA content of 96.4%.

The organic solutions were prepared by dissolving the extractant in kerosene (mainly paraffinic and naphthenic hydrocarbon in C₁₀-C₁₄ range).

The stock solutions of samarium, europium, gadolinium and terbium were prepared by dissolving their oxides in hydrochloric acid at room temperature with the acidity being adjusted for the conditions of the experiments.

The effect of equilibration time on the extraction of Sm, Eu, Gd and Tb using 1.0 mol/L HEHEPA was studied and it was observed that under the given experimental conditions a minimum of 3 min time is required for attaining the limiting extraction. It was checked that prolonged shaking does not affect the results.

Equal volumes (10 ml) of aqueous and organic solutions of known concentrations were mixed and shaken for 10 min in stoppered glass tubes at 298 K, then allowed to settle for at least 1 h.

The RE concentrations were determined in the aqueous phase by ICP-AES and the metal ions concentration in the organic phase was calculated using a material balance technique. All the experiments were performed in duplicate as a check on the experimental technique and precision.

The distribution of single RE (ranging from 0.01 and 0.21 mol/L) between organic and aqueous phases was examined as a function of the hydrogen ion concentration and the metal concentration.

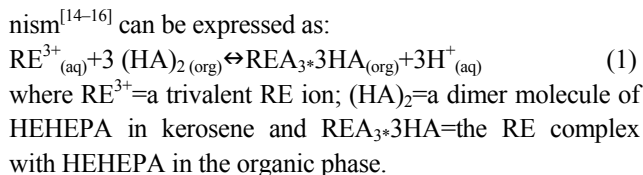
In order to determine the best conditions of extraction, we also carried out extraction data of artificial mixed solutions (Sm-Gd, Eu-Gd, Gd-Tb): aliquots of the aqueous phase (after reaching equilibrium) were sampled to determine simultaneously the concentration of middle RE. The total rare earth concentration of mixed solution was investigated from 7.1×10^{-3} mol/L to 0.16 mol/L.

The separation factors $\beta_{RE1/RE2}$, indicating the effectiveness in the separation of the elements, were calculated by the ratio between the distribution coefficient D (defined as the ratio between the concentration of the RE elements in the organic phase and that in the aqueous phase at the equilibrium) obtained at the same time of the RE element 1 and the element 2.

2 Results and discussion

HEHEPA is a liquid cation-exchanger, the extracted metal being exchanged by the hydrogen ion in the hydroxyl group; Fig. 1 shows the structural formula.

For the extraction of lanthanides with an acidic organophosphorous extractant, the proposed ion-exchange mechanism^[14-16] can be expressed as:



The extraction of the RE depends on the initial acidity and on the initial metal concentration provided the extractant concentration is constant.

The extraction values (in %) of chloridric solution of trivalent Sm, Eu, Gd and Tb have been determined at 298 K using 1.0 mol/L HEHEPA in kerosene varying metal concentrations and pH.

The results are given in Figs.2-5: as expected observing Eq. 1, increasing the metal concentration and maintaining constant the concentration of extractant, the RE extraction decreases: this is due to the fact that, at the equilibrium, the concentration of the available extractant and the pH at the same time decrease, and moreover chloride ions can co-ordinate with RE. When the pH reaches values less than 0.5, the RE extraction drops to nearly zero.

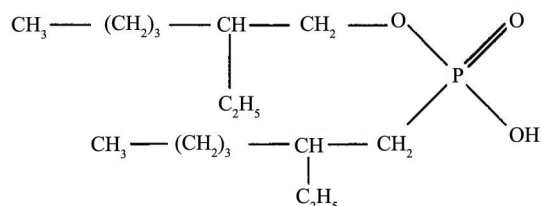


Fig. 1 Structural formula of the 2-ethylhexyl 2-ethylhexylphosphonic acid

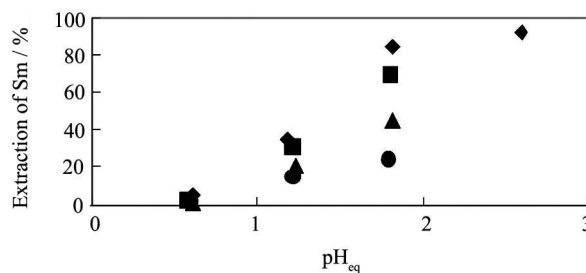


Fig. 2 Effect of the acidity on the extraction of Sm at 298 K
 ◆ C_{Sm}: 0.04 mol/L; ■ C_{Sm}: 0.05 mol/L; ▲ C_{Sm}: 0.10 mol/L;
 ● C_{Sm}: 0.21 mol/L

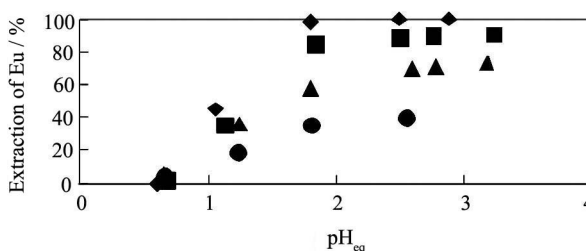


Fig. 3 Effect of the acidity on the extraction of Eu at 298 K
 ◆ C_{Eu}: 0.01 mol/L; ■ C_{Eu}: 0.05 mol/L; ▲ C_{Eu}: 0.09 mol/L;
 ● C_{Eu}: 0.16 mol/L

Fig. 6 shows that, at constant pH, Eu and Gd have a similar behaviour, while Tb and Sm have rather different extraction coefficients.

Tables.1–3 show β coefficients varying in a non-linear fashion compared to the increment of total RE concentration in the feed solution at a constant acidity: it can be presumed that RE mole fractions influence the extraction process and the ion exchange mechanism during the simultaneous extraction is influenced by other factors which need further investigation. We have not considered the $\beta_{RE1/RE2}$ at $\text{pH} < 1$ because at low pH values (Figs. 2–6), the extraction coefficients are low and consequently the values of distribution coefficients D (utilized to calculate β) are susceptible of great error.

These data show that the Gd-Eu separation using HEHEPA is more difficult than Gd-Sm and Eu-Tb (as expected observing Fig. 6 and considering that they are adjacent elements).

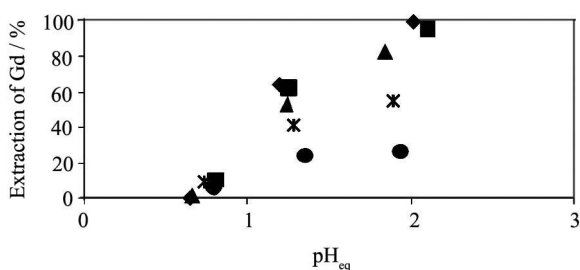


Fig. 4 Effect of the acidity on the extraction of Gd at 298 K

◆ C_{Gd} : 0.01 mol/L; ■ C_{Gd} : 0.03 mol/L; ▲ C_{Gd} : 0.05 mol/L;
* C_{Gd} : 0.10 mol/L; ● C_{Gd} : 0.21 mol/L

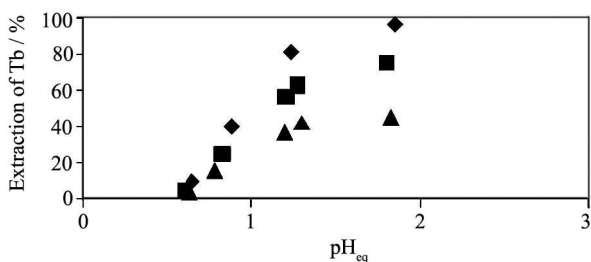


Fig. 5 Effect of the pH on the extraction of Tb at 298 K

◆ C_{Tb} : 0.04 mol/L; ■ C_{Tb} : 0.09 mol/L; ▲ C_{Tb} : 0.19 mol/L

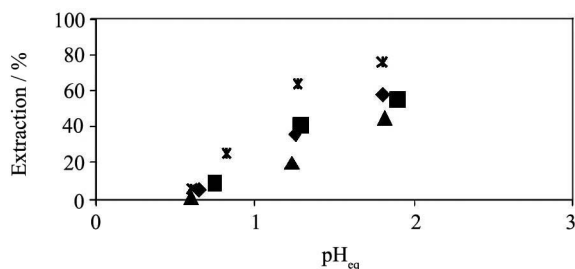


Fig. 6 Extraction of middle rare earths 0.10 mol/L as function of acidity at 298 K

* Tb; ■ Gd; ◆ Eu; ▲ Sm

Table 1 Separation factors obtained from the simultaneous extraction of Gd and Sm

pH_{eq}	$\beta_{\text{Gd/Sm}}$		
	4.0×10^{-2} mol/L Gd	2.7×10^{-3} mol/L Sm	5.0×10^{-2} mol/L Sm
1.2	3.3	4.6	3.5
1.8	3.3	5.1	3.3

Table 2 Separation factors obtained from the simultaneous extraction of Gd and Eu

pH_{eq}	$\beta_{\text{Gd/Eu}}$					
	4.0×10^{-2} mol/L Gd			9.0×10^{-2} mol/L Gd		
	3.7×10^{-3} mol/L Eu	1.5×10^{-2} mol/L Eu	6.8×10^{-2} mol/L Eu	5.0×10^{-3} mol/L Eu	1.6×10^{-2} mol/L Eu	7.3×10^{-2} mol/L Eu
1.2	1.5	1.5	1.2	1.6	1.5	1.7
1.8	1.5	1.6	1.1	1.5	1.4	1.6

Table 3 The separation factors obtained from the simultaneous extraction of Eu and Tb

pH_{eq}	$\beta_{\text{Tb/Eu}}$					
	3.7×10^{-3} mol/L Eu			3.4×10^{-2} mol/L Eu		
	3.3×10^{-3} mol/L Tb	1.4×10^{-2} mol/L Tb	3.7×10^{-2} mol/L Tb	3.4×10^{-3} mol/L Tb	1.4×10^{-2} mol/L Tb	3.4×10^{-2} mol/L Tb
1.2	11.1	9.0	8.6	9.3	8.7	8.9
1.8	*	11.5	8.9	8.3	9.8	9.7

* This value is not reported since, at the indicated concentrations, both Eu and Tb are completely extracted.

On the base of these results, we can confirm an order of extractive ability of middle RE by 1.0 mol/L HEHEPA in kerosene: $\text{Tb} > \text{Gd} > \text{Eu} > \text{Sm}$.

The increase in the extraction from Sm to Tb can be explained by the increase in the acidity of these elements, related to the systematic decrease in the ionic radii of the RE elements (the well-known “lanthanide contraction”, which increases with the atomic number in the lanthanide series)^[17].

The size difference between adjacent members of the RE elements in a given state of oxidation is very small, and in the particular case of Eu^{3+} - Gd^{3+} the size difference is almost negligible: this can explain the results of Table 2 that shows small separation coefficient.

3 Conclusion

The extraction of individual middle RE elements and the separation of mixed middle RE elements (simulating the waste from NiMH batteries) from chloride media was investigated using HEHEPA in kerosene as an extractant.

The extraction occurred via a proton exchange reaction

and the results clearly demonstrated that it was possible to separate the middle RE from each other using 1.0 mol/L HEHEPA: the order of the extractive ability of extractant in chloride media was: Tb>Gd>Eu>Sm.

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