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# Solid–Liquid Extraction of Rare Earths with 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester Using Paraffin Wax as Solvent

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## Abstract

The solid–liquid extraction of rare earths with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507, HL) has been studied in molten paraffin wax from hydrochloric acid. The mechanism of extraction was investigated by a slope analysis method and the composition of the extracted complex was further determined by a saturation volumetric method. The gelatinous extracted complex was separated from the wax phase and studied by IR spectroscopy. From the IR spectra the chemical bonding in the extracted complex is postulated. The extraction constants $K_{ex}$ of fifteen rare earths have been evaluated. The plots of log $K_{ex}$ and pH ($E = 50\%$) *versus* atomic number $Z$ show a tetrad effect. The mean separation factor of adjacent rare earths is 2.78. All experimental results agree with those of the extraction with P507 in *n*-dodecane. This proves that the same principles can be applied to both solid–liquid and liquid–liquid extraction systems. But the extraction using molten wax as solvent has some merits, such as accuracy, simplicity, rapidity, safety and economy.

## Introduction

In solid–liquid extractions, paraffin wax, naphthalene and diphenyl, etc., which are solid at room temperature, are used as solvents in the molten form to dissolve the extracting agent and extract the metal ions from the aqueous phase as the ordinary solvents. After equilibrium the cooling organic phase separates out in a solid form. This method has been used for separation in analytical chemistry for a few years [1–3], but the extraction mechanism of such a system has rarely been reported [4]. The liquid–liquid extraction of rare earths by P507 has also been systematically studied [5]. However, in a solid solvent such as paraffin wax, the extraction behavior of P507 for rare earths has not yet been studied. The extraction of rare earths (RE) by P507 in wax from hydrochloric acid is described in detail in this paper. It is proved by experiment that all the principles of liquid–liquid extraction can be applied to solid–liquid extraction. Solid–liquid extraction, with the exception of the higher temperature required for melting, is more convenient and more efficient than liquid–liquid extraction. Wax as a solvent is cheap, non-poisonous, non-volatile and easy to recover. It is almost an ideal solvent for extraction. Kojima *et al.* [1, 4] have mentioned that the solid phase tends to adhere to the beaker wall, but we have avoided such a fault by using an appropriate phase ratio (1:30). Solid–liquid extraction is a new convenient method for extraction study. Of course, this method has some restrictions, e.g., both the extracting agent and the extracted complex must be soluble in the molten solvent. Besides, this method can only be applied to extractions at low concentrations.

## Experimental

### *Reagents*

Paraffin wax, melting point (m.p.) 58–60 °C was used. P507 was purified by a copper salt purification method [6]. A product purity of more than 97% was determined by potentiometric titration. Rare earth solutions were prepared from rare earth oxides (99.99%) dissolved in hydrochloric acid and diluted to the required volume. Other reagents were of A.R. grade.

### *Methods*

30 ml of $1 \times 10^{-4}$ M $RECl_3$ solution and accurate amounts of wax and P507 were added to a small beaker and stirred vigorously with a magnetic stirrer at 70–80 °C for 5 min (it was found by experiment that the equilibrium can be reached within 1 min). The cooling wax phase solidified, floated on the surface and naturally separated from the aqueous phase.

The concentration of rare earth in the aqueous phase was analysed and the concentration in the organic phase was calculated by subtracting the concentration in the aqueous phase from the original concentration in the aqueous phase before extraction. All data are the average values of at least two experimental results.

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### *Analysis*

Concentrations of rare earths were determined either volumetrically by EDTA titration with xylenol orange as indicator or spectrophotometrically by CPA-mN [7] according to their concentration. The concentration of hydrogen ion was determined volumetrically by NaOH titration with bromthymol blue as indicator.

### *Instruments*

721 Spectrophotometer (Shanghai 2nd Analytical Factory), FT-IR (170 SX) spectrometer (Nicolet, USA), and PH S-3 pH meter (Shanghai 2nd Analytical Factory) were used.

## Results and Discussion

### *Extraction Mechanism by Slope Analysis Method*

Generally, the mechanism of extraction of rare earths with an acidic organophosphoric ester in less acidic medium is considered to be cation exchange. The mechanism of the system $RE^{3+}$ ($1 \times 10^{-4}$ M)/HCl, NaCl (1 M)/P507 (0.6536 M)-wax was studied by the slope analysis method. We have determined the distribution ratio $D$ of fifteen rare earths (including yttrium but not promethium) with various pH values (other conditions were kept constant). The plot of log $D$ *versus* pH (70–80 °C) was found to be a straight line. Linear regression by the programmable calculator TI 59 gave estimates of the slopes of fifteen lines as 2.8 to 3.1 (Fig. 1).

The distribution ratios of $Eu^{3+}$, $Gd^{3+}$, $Tb^{3+}$ and $Dy^{3+}$ of the system $RE^{3+}$ ($1 \times 10^{-4}$ M)/HCl (0.1023 N), NaCl (1 M)/P507-wax with various concentrations of P507 in wax were also determined. By plotting log $D$ against log $[H_2L_2]$ the slope was also found to approach 3 (Fig. 2).

Thus the mechanism of solid–liquid (wax–water) extraction of $RE^{3+}$ with P507 is found to be cation exchange, in agreement with liquid–liquid extraction. The extraction reaction of rare earths can be written as follows:

$$RE_a^{3+} + 3(H_2L_2)_o = RE(HL_2)_{3o} + 3H_a^+$$

the subscripts o and a denote species in the organic phase and aqueous phase respectively.

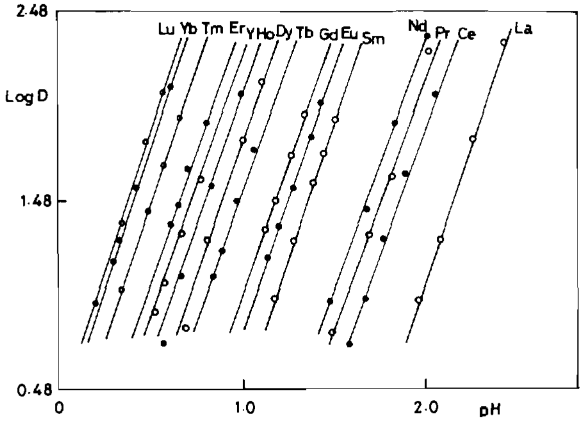


Fig. 1. Rare earths extraction by P507 at various acidities, 70–80 °C, Na(H)Cl = 1 M.

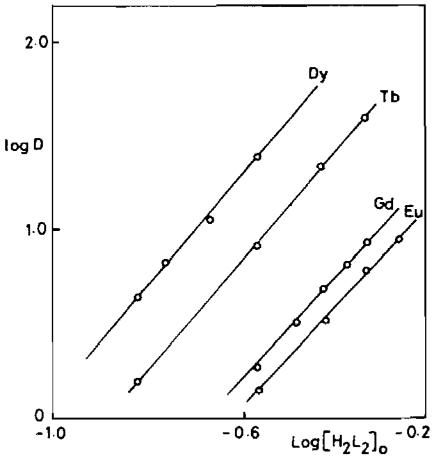


Fig. 2. Rare earths extraction by P507 at various concentrations of the extractant, 70–80 °C, Na(H)Cl = 1 M.

### *Composition of Extracted Complex by Saturation Volumetric Method*

P507 (0.2 g) was dissolved in 1.5 g wax and $Nd^{3+}$ was extracted from aliquots of 30 ml 0.02440 M $NdCl_3$ solution (pH = 2) repeatedly until the concentration of $Nd^{3+}$ in the aqueous phase remained constant. The organic phase was saturated. After each extraction the aqueous phase was analysed by EDTA titration (Table I) and discharged. Then the mole ratio of the extracting agent (HL) in the organic

TABLE I. Relationship between the Amount of $Nd^{3+}$ Extracted and the Number of Extractions in the Saturation Volumetric Method ($C_{Nd^{3+}} = 0.02440$ M)

| Number of extractions | Concentration of $Nd^{3+}$ after extraction (M) | Quantity extracted (mol) | Total quantity extracted (mol) |
|---|---|---|---|
| 1 | 0.02210 | $0.069 \times 10^{-3}$ | |
| 2 | 0.02295 | $0.0435 \times 10^{-3}$ | |
| 3 | 0.02438 | 0 | $0.1125 \times 10^{-3}$ |

phase and the total $Nd^{3+}$ extracted was estimated to be 5.8:1, that is the mole ratio in the extracted complexes – $HL:Nd^{3+} = 6:1$, approximately. From the slope analysis method the coefficient of $[H^+]$ was found to be close to 3, indicating that HL exists as a dimer in the solvent wax just as in other nonpolar solvents.

The saturated organic phase was back-extracted with 1 N $HNO_3$ and the chloride ion was detected in the back-extraction aqueous solution with $AgNO_3$. The result was negative, further confirming that the composition of the extracted complex is $Nd(HL_2)_3$, in agreement with the slope analysis method.

In our experiment we observed that when the organic phase was saturated by neodymium a purplish gelatinous solid appeared, and after cooling it solidified with wax. The purplish gel is the extracted complex of neodymium and P507. The same process was applied to the heavy rare earths Yb and Tb. After the first extraction the mole ratio already reached 4.4:1. Perhaps part of the P507 dimer dissociated when the load of P507 increased. This should be studied further.

### Bonding in the Extracted Complex by IR Spectroscopy

The IR spectra of the neodymium complex are given in Fig. 3. By comparing the IR spectra of the neodymium complex with the parent compound P507, some obvious differences are shown:

(1) $H_2O$ adsorption bands at 3500–3000 $cm^{-1}$ were observed for the complex.

(2) The broad absorption bands (2600, 2314, 1666–1697 $cm^{-1}$) of the associated OH group existing in the parent ligand disappeared in the complex.

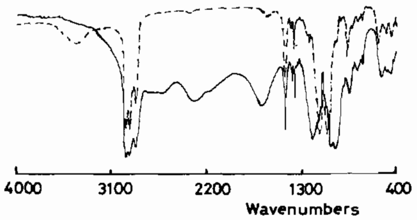
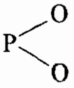
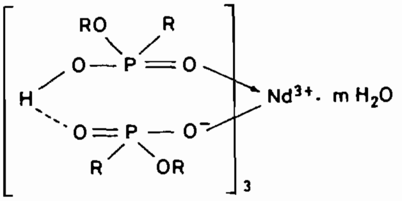


Fig. 3. IR spectra of P507 (solid line) and its complex with neodymium (dashed line) (KBr pellets).

(3) With the disappearance of the original P=O sharp absorption (1196 $cm^{-1}$), P–O–C and P–C absorption (1036, 985 $cm^{-1}$) in the complex, the asymmetric absorption (1132 $cm^{-1}$) and the symmetric absorption (1048 $cm^{-1}$) of  $P{<}^{O}_{O}$ occurred. This indicates that the ligand and metal are bonded through P=O and $P–O^-$ to form the complex. So the chemical bonding in the neodymium complex may be considered as follows:



### Back-extraction

We have back-extracted the four extractants of $Eu^{3+}$ in the former experiment (extraction with various concentrations of extracting agent) with 1 N HCl (Table II). Relative deviation of this experiment is as follows:

$$\frac{0.230 - 0.225}{0.225} = +2.2\% \ (<5\%)$$

Back-extraction only once with 1 N HCl can recover all the rare earths extracted. Percentage recovery is up to 100% (for $Nd^{3+}$, $Yb^{3+}$, $La^{3+}$). These are very satisfactory results.

We also carried out another interesting experiment. The above wax phase was taken after back-extraction to extract $Nd^{3+}$ from another fresh aqueous phase and back-extracted again to recover the wax phase. Such a process can be repeated again and again. The extraction ability of the extractant remains the same (Table III).

The results indicated that the extractants (P507 and wax) can be used repeatedly without loss of ability of extraction. That is the main advantage of solid–liquid extraction.

TABLE II. Results of Back-extraction

| Amount of P507 (g) in extraction | Absorbance of aqueous phase | | |
|---|---|---|---|
| | *A* (after extraction) | *A'* (after back-extraction) | Total[a] *A* + *A'* |
| 0.5000 | 0.177 | 0.115 | 0.232 |
| 0.4000 | 0.135 | 0.092 | 0.227 |
| 0.3010 | 0.165 | 0.067 | 0.230 |
| 0.2000 | 0.197 | 0.033 | 0.230 |

[a] Absorbance of the initial aqueous phase before extraction equals 0.225.

TABLE III. The Extractant Repeatedly Used for Extraction

| Number of extractions | Absorbance of aqueous phase | | |
|---|---|---|---|
| | $A$ (after extraction) | $A'$ (after back-extraction) | Total[a] $A + A'$ |
| 1 | 0.197 | 0.033 | 0.230 |
| 2 | 0.188 | 0.036 | 0.224 |
| 3 | 0.190 | 0.037 | 0.227 |

[a] Absorbance of the initial aqueous phase before extraction equals 0.225.

TABLE IV. The Equilibrium Constants and Separation Factors of Rare Earths Extracted by P507

| Element | $\log K_{ex}$ | $\beta_{Z+1/Z}$ |
|---|---|---|
| La | −3.17 | 6.47 |
| Ce | −2.36 | 2.25 |
| Pr | −2.00 | 1.47 |
| Nd | −1.84 | 1.64 |
| Pm | (−1.62)[a] | 5.88 |
| Sm | −0.85 | 2.04 |
| Eu | −0.54 | 1.28 |
| Gd | −0.43 | 5.32 |
| Tb | 0.29 | 2.46 |
| Dy | 0.68 | 1.27 |
| Ho | 0.79 | 2.34 |
| Er | 1.16 | 3.20 |
| Tm | 1.66 | 2.19 |
| Yb | 2.00 | 1.11 |
| Lu | 2.05 | |
| Y | 0.99 | |

[a] $\log K_{ex}$ of Pm is the extrapolated value.

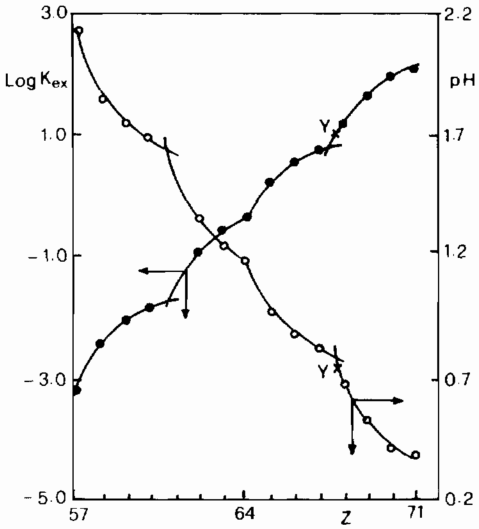


Fig. 4. Relationship between the extraction equilibrium constants and pH ($E = 50\%$) and atomic numbers of rare earths in extraction by P507.

### *Regularities of Variation of the Extraction Equilibrium Parameters with the Atomic Number of the Rare Earths*

Using the calculator TI-59 the extraction equilibrium constants $K_{ex}$ and their statistical mean value for each rare earth were estimated from the experimental data in Fig. 1. The results are listed in Table IV. Also from the experimental data in Fig. 2 the mean $\log K_{ex}$ values of $Eu^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$ were calculated to be −0.65, −0.51, 0.16 and 0.52 separately, very close to those in Table IV. The separation factors $\beta_{Z+1/Z}$ of adjacent rare earths were also calculated from their $\log K_{ex}$ values. The plot of $\log K_{ex}$ of fifteen rare earths against atomic number $Z$ reveals an obvious tetrad effect (Fig. 4). Y is located between Ho and Er due to the appropriate ionic radius. The average separation factor of adjacent rare earths $\beta_{Z+1/Z}$ equals 2.78, only slightly lower than the value in ref. 5. The regularities described above are all in agreement with those stated in ref. 5, proving that the same principles can be applied to both solid–liquid and liquid–liquid extractions.

In this experiment the phase ratio $R = 1/30$. At 50% extraction (extraction ratio $E = 50\%$), from the following relationships:

$$C_{o(RE^{3+})} V_o = C_{a(RE^{3+})} V_a$$

$$C_o/C_a = V_a/V_o$$

one can obtain:

$$D(E = 50\%) = 1/R = 30$$

$$\log D = \log 30 = 1.4771$$

The tetrad grouping is also shown by plotting the pH values at $E = 50\%$ against atomic numbers of all the rare earths. As far as we know, the tetrad effect between the atomic numbers of rare earths and the pH ($E = 50\%$) has not yet been reported.

## Supplementary Material

Routine data have been retained by author Cheng Li.

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## References

1 T. Kojima, Y. Shigetomi, H. Kamba, H. Iwashiro, T. Sakamoto and A. Doi, *Analyst, 107,* 519 (1982).
2 Y. Shigetomi and T. Kojima, *Talanta, 27,* 1079 (1980).
3 Z. Xu and L. Dai, *Fenxi Huixue, 13,* 784 (1985).
4 T. Kojima, *Bull. Chem. Soc. Jpn., 57,* 198 (1984).
5 E. Ma, X. M. Yan, S. Wang, H. Long and C. Yuan, *Sci. Sin., 24,* 1235 (1981).
6 C. Peng, Y. Ji, A. Lu and D. Liu, *Fenxi Huixue, 8,* 318 (1980).
7 C. Hsu, C. Hu, X. La and L. Pan, *Anal. Chim. Acta, 124,* 177 (1981).