

Solvent Extraction Study for 4f Series Elements by bis(2-ethylhexyl) Phosphoric Acid

C. T. Rhee, H. M. Cho and S. H. Kim

Department of Chemistry, Inha University

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Abstract

A solvent extraction technique, using bis (2-ethylhexyl) phosphoric acid, (HDEHP), as the extractant, was employed to examine some characteristic difference between lighter and heavier parts of 4f series. Some difference in temperature dependencies of the distribution ratios between the two groups were observed for the aqueous systems of H_2SO_4 and HCl. This experimental results were tentatively assigned as the difference in the ability of formation of inner coordination complex with HDEHP derived from the lanthanon contraction.

요 약

重希土와 輕希土間의 特性上의 差異를 보기 위하여 HDEHP 를 溶媒로 使用하여 HCl, H_2SO_4 및 HNO_3 水溶液으로 부터 抽出해 보았다. H_2SO_4 와 HCl 系에서 重希土와 輕希土間에 나타나는 抽出率의 溫度依存性은 서로 상이함을 알았으며 이것은 抽出種인 配位錯物形成에 있어 HDEHP 의 配位圈 차이에 差異 때문으로 해석된다.

Introduction

Even though many works have been published connected to the lanthanide elements and their compounds during past few decades and even, so called, "tetrad effect" caused by the faint nephelauxetic effect of the 4f electrons during the process of inner coordination complex formation have investigated recently, there are still many unknown factors to be studied in the formation process of extractable species from aqueous species.

The lanthanide ions are strongly electro-positive and have comparatively large ionic

radii. The shrinkage of the ionic radii as the 4f sub-shell is filled is estimated as around 22%. The influence of the shrinkage affects not only the ionic size itself but also the surface charge density around the cation, and the influence on coordination number and coordination geometry is unifying concept in the coordination chemistry of the lanthanide ions.

Experiments

Source of materials; HDEHP, supplied by BDH chemicals Ltd, England, was further purified and the purity was checked according

to the same method as in previous work.¹⁾ Each radioactive tracers were prepared by neutron irradiation at Korean Atomic Energy Research Institute. The target materials were >99.99% purity grade and were received from Research Chemicals Inc. U. S. A. . Other chemicals including toluene which was used as diluent in organic phase were all special grade.

Extraction apparatus; Water jacketed double reaction cell(the volume of inner cell was ~10ml) was used for controlling the reaction temperature. This cell was mounted on a motor driven shaking machine and the shaking rate was controlled by means of a transformer. The shaking speed was always adjusted to 60 ± 3 cycles per minutes. The temperature was controlled by continuous water flowing through the cell jacket from the thermostat. The shaking period was 60 min. except the case of extraction rate determination.

Extraction and Radioassay; 2.5ml each of pre-equilibrated organic phase and aqueous phase was taken in the cell. The tracer was added just prior to start actual extraction operation. After shaking for pre-determined period, it was transferred into centrifuge cell immediately and the both phases were separated by double centrifuge operation. Every possible caution was taken to avoid fluctuation in the condition throughout the experiments such as temperature, shaking condition and centrifugal operation. Distribution ratio was determined by measuring the gamma activities of equal volume of both phases using NaI(Tl) well type scintillator.

Results and Discussion

The distribution ratios (D) of La, Nd,

Sm, Eu, Gd, Tb, Er and Lu at 20°C and 35°C for the aqueous phase of various HCl concentrations (0.1 N, 0.2N, 0.3N and 0.4N) are shown in Table 1. The concentration of HDEHP in Toluene for each experiments was adjusted to get proper D value. Examining the results on Table 1, the D values at 35°C are essentially greater than that at 20°C for La to Gd. On the contrary, this general tendency is reversed for the heavier lanthanons for smaller HCl concentrations (<0.3N). An inverse third-power dependence on HCl concentration was fairly well kept for the lighter lanthanons at 20°C and 35°C but less than third power was observed for the heavier lanthanons at 35°C. Lu, the last member of lanthanon series, was chosen for the further study on the said interesting tendency.

Table 2 and Table 3 are the results of results of Lu extraction for the aqueous system of H₂SO₄ and HNO₃ solution respectively. For the H₂SO₄ system the same tendency as the case of HCl system was observed but the HNO₃ system did not follow the same tendency and the D value decreased all the way through according to increasing temperature. Fig.1-a and -b shows the variation mode of D_t/D_{60} according to extraction period for Lu for three different aqueous systems of 0.2N HCl, 0.4N HCl and 0.4N HNO₃ at 20°C and 35°C respectively. Here, D_{60} designates the D value at 60 min. shaking period for the system and D_t designates the D value at each corresponding shaking period for the same system. Thus, larger the value of D_t/D_{60} , the extraction is nearer to the final equilibrium state for the system. As can be seen from the graph the extraction rate is much greater for the system of HNO₃ than that for the system of HCl,

Table 1. D values of La, Nd, Sm, Eu, Gd, Tb, Er, and Lu at 20°C and 35°C for the aqueous system of various HCl concentrations.

| Element | | HCl(N) | | | | HDEHP(M) in Toluene |
|---------|------|--------|-------|------|-------|---|
| | | 0.1 | 0.2 | 0.3 | 0.4 | |
| La | 20°C | 2.98 | 0.37 | 0.11 | 0.046 | 1.52×10° |
| | 35°C | 3.09 | 0.139 | 0.12 | 0.050 | |
| Nd | 20°C | 15.04 | 2.10 | 0.62 | 0.26 | 1.22×10° |
| | 35°C | 17.67 | 2.23 | 0.65 | 0.28 | |
| Sm | 20°C | 6.16 | 0.74 | 0.22 | 0.09 | 6.08×10 ⁻¹ |
| | 35°C | 6.54 | 0.78 | 0.24 | 0.10 | |
| Eu | 20°C | 14.77* | 1.85* | 1.98 | 0.64 | 6.08×10 ⁻¹ (for*), 9.12×10 ⁻¹ |
| | 35°C | 15.38* | 1.92* | 2.02 | 0.66 | |
| Gd | 20°C | 38.30 | 4.45 | 1.22 | 0.56 | 6.08×10 ⁻¹ |
| | 35°C | 39.65 | 5.02 | 1.43 | 0.57 | |
| Tb | 20°C | — | 14.62 | 3.54 | 1.80 | 6.08×10 ⁻¹ |
| | 35°C | — | 14.02 | 3.47 | 1.80 | |
| Er | 20°C | — | 22.45 | 5.50 | 2.52 | 3.04×10 ⁻¹ |
| | 35°C | — | 21.78 | 6.47 | 2.86 | |
| Lu | 20°C | 80.83 | 9.30 | 2.61 | 1.10 | 6.99×10 ⁻² |
| | 35°C | 67.17 | 8.80 | 2.84 | 1.20 | |

Table 2. D value of Lu at 20°C and 35°C for the aqueous systems of 0.1N, 0.2N, 0.3N and 0.4N H₂SO₄

| Element | | H ₂ SO ₄ (N) | | | | HDEHP(M) in Toluene |
|---------|------|------------------------------------|-------|------|------|-----------------------|
| | | 0.1 | 0.2 | 0.3 | 0.4 | |
| Lu | 20°C | 101.02 | 12.28 | 3.34 | 1.29 | 7.60×10 ⁻² |
| | 35°C | 91.23 | 11.18 | 3.72 | 1.33 | |

Table 3. D values of Lu at 20°C and 35°C for the systems of 0.1N, 0.2N, 0.3N and 0.4N HNO₃

| Element | | HNO ₃ (N) | | | | HDEHP(M) in Toluene |
|---------|------|----------------------|-------|------|------|-----------------------|
| | | 0.1 | 0.2 | 0.3 | 0.4 | |
| Lu | 20°C | 99.22 | 12.44 | 3.63 | 1.47 | 7.60×10 ⁻² |
| | 35°C | 80.29 | 9.05 | 2.56 | 1.13 | |

Among the two systems of HCl, the D_i/D_{60} value for the case of 0.2N is still greater than the case of 0.4N. And, for every extraction system, the D_i/D_{60} value at 35°C is greater than the corresponding value at 20°C.

It could be thought as the extracted species in the organic phase were different chemical

compositions according to the aqueous systems and this might cause the observed different tendencies. Even though some possible suggestion (formation of rare earth chlorocomplexes with solvent molecules) was reported²⁾ to explain the increasing distribution ratio with increasing HCl concentration

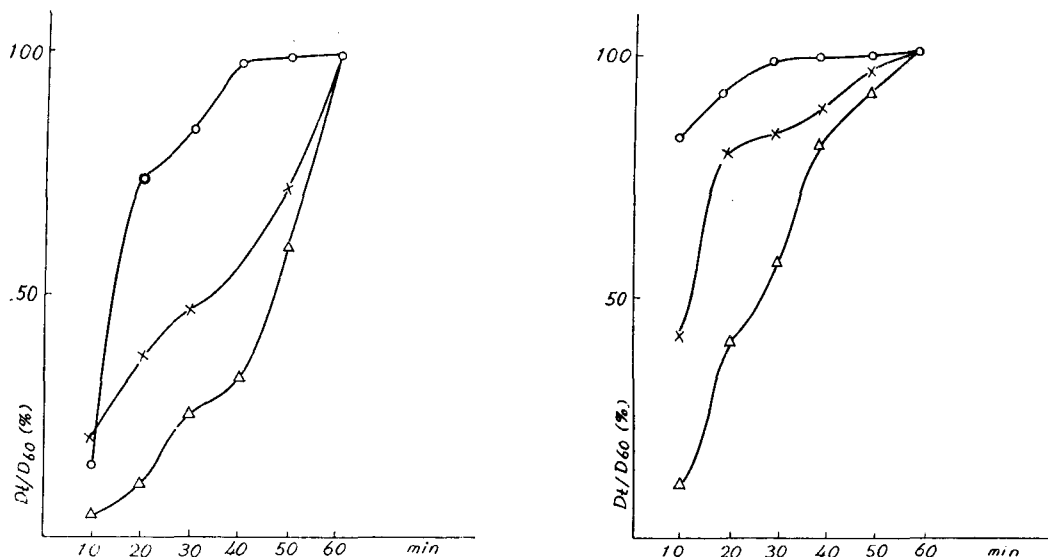


Fig. 1 Variation mode of D_t/D_{60} of Lu for the aqueous system of 0.2N HCl, 0.4N HCl and 0.4N HNO₃ at a) 20°C and b) 35°C

for the extraction system of rare earth chloride with HDEHP, (this suggestion was also supported by the quantitative analysis of the chlorine concentration in organic phase and in aqueous phase by T. Harada et al³⁾) this possibility is excluded by several workers experimental results.⁴⁻⁶⁾ at least, for the systems of anion concentration as low as present study. The authors also performed some experiments using radioactive tracer of chlorine to check such possibility of chlorocomplex formation in organic phase. The results are shown in Table 4. Among the three values of D_{Cl} in Table 4 (D_{Cl} designates the D value of chlorine) the lowest value was obtained for the system of 0.4N HCl - 0.01M LuCl₃. The relatively higher values of D_{Cl} for the other two systems can be understood as the distribution of HCl in the organic phase forming $[HCl \cdot nHDEHP]$ as reported by T. Harada et al³⁾.

The next approach might be done with the chemical species formed in the aqueous phase. R. J. Sochacka et al reported⁷⁾ that

there was no correlation among their data obtained from their reversed phase chromatograph experiments between the effective height of the theoretical plate and the degree of association of rare earth cations with various mineral acid in the aqueous phase. The order of increasing association in the aqueous phase was $HClO_4 < HCl < HNO_3 < H_2SO_4$ and the order of the plate height was $HNO_3 < HClO_4 < HCl \approx H_2SO_4$. They suggested some plausible model, even though they could not offer any confirmative verification, to explain these contradiction. Upon their opinion, the height of the plate should be related to the kinetic effect resulting from the kinetic stability of the complex and this stability is not always related to the thermodynamical stability, and the association between rare earth cation and the ClO_4^- or NO_3^- is caused by hydrogen bonding between water molecules in the first coordination shell of the cation and the in the second (outer) coordination shell. On the contrary, the Cl^- and SO_4^{2-} anions would

Table 4. Distribution ratio of chlorine for various aqueous systems.

| Exp. No. | aqueous phase | D_{Cl} |
|----------|-------------------------|----------|
| 1. | 0.4 N HCl | 0.022 |
| 2. | 0.4N HCl-0.01M $LuCl_3$ | 0.008 |
| 3. | 0.4 N HCl-0.2M NaCl | 0.017 |

Organic phase; 1.52×10^{-1} M HDEHP in Toluene

be able to replace the water molecules in the inner coordination shell of the cation. The author found that such like model could be used to explain the present results. As clearly understood, the ionic radius are getting smaller according to lanthanon contraction and, on the contrary, the size of the hydrated rare earth cation or the hydration number are getting larger even though the coordination number of heavier lanthanons are smaller than the lighter group. Generally speaking it is fairly difficult to estimate the influence of the extraction temperature because of the every factors such as forms of chemical species, activity of the components, dissociation of the solvent, hydration degree of the ions, distribution coefficients etc, which are related, more or less, to the extraction ratio. But for the present case the different tendencies between lighter and heavier parts of lanthanon series may be treated as any inherent characteristical difference between them. There are many works published⁸⁻¹³⁾ related to thermodynamical treatment for the rare earth complexes with inorganic ligands, and some common derivations were derived concerning about the sign and magnitude of the enthalpy change and entropy change related to inner and outer sphere coordination model even though there are still appreciable disc-

repancies among their data and conclusions.

The concept of iceberg, i.e., model of ionic solutions proposed by Frank et al¹⁴⁾ was the fundamental basis used by them. Thus, in general, the net positive enthalpy change and positive entropy change can be related to inner-sphere complex formation and net negative enthalpy and entropy change can be related to outersphere complexes or ion pair association. The author likes to suggest another approach for the present work. The main differences between the works published and the present discussion are; First, the chemical species newly formed are the extractable species from the species already formed in aqueous solution they could be free ion, ion pair, inner or outer-sphere complexes with inorganic ligands, or probably their mixtures. Second, the ligands which enter or replace inorganic (including water molecules) ligands are large and hydrophobic solvent molecules. Upon these assumption, the formation of extractable species of lanthanons from the aqueous species could be classified into two categories as follows:

I) all or part of the solvent ligand occupy the inner (primary) sphere of the cations replacing all or part of coordinated water molecules and/or inorganic ligands (if exist in that sphere).

II) solvent ligand occupy only the outer (secondary) sphere of the cations replacing all the water molecules and/or inorganic ligands in that sphere. For the category I), the extraction process will be endothermic and the sign of ΔS will be positive but for the category II) it will be exothermic and the sign of ΔS will be negative. These are based on the same reason as the formation of complexes from hydrated cations with

inorganic ligands. Upon geometrical consideration, there will be severe restrictions in coordinating the bulky solvent ligand, such as HDEHP, to small central cations and this effect will be getting pronounced going to higher atomic number in lanthanons. Moreover, the size and the regularities of hydration zone are getting larger progressively because of the increasing effective charge density of the central ions. With these considerations, it is assumed that HDEHP ligand (even not all of them) can occupy the position of inner sphere of the lighter lanthanon ions but cannot enter into the inner sphere, as a general rule, of the heavier rare earth cations. But, as an exception, the HDEHP ligand (at least one of them) can enter into the inner sphere if the position is occupied by replaceable inorganic ligands. If the above mentioned tentative assumption is allowed the present experimental results can be explained. The case of the lighter lanthanons and Lu at higher acidity ($\geq 3N$) of HCl and H_2SO_4 are belong to category I) and Lu at lower acidity ($\leq 2N$) of HCl and H_2SO_4 and all the case of HNO_3 are belong to category II). Of course the dividing of the acidity is for conventional purpose and the two forms should coexist at any acidity and the ratio between them may be varied according to the change of acidity.

The temperature dependence of \bar{z} Lu for four aqueous systems of 0.2N HCl, 0.3N HCl, 0.3N HCl-0.2M $NaClO_4$, and 0.3N HCl-0.2M NaCl are shown in Table 5. As can be seen from the table, the D values decrease according to increasing temperature for the systems of 0.2N HCl and 0.3N HCl-0.2M $NaClO_4$ and reverse tendencies for the other two systems. The plots of $\log D$ against $1/T$ are linear for the two systems of 0.2N HCl and 0.3N HCl. To evaluate the enthalpy change associated with the extraction process the following equation was used:

$$\Delta \log D / \Delta 1/T = -H^\circ / 2.303R$$

~ -0.27 Kcal/mole for 0.2N HCl system and ~ 0.30 Kcal/mole for 0.3N HCl system were obtained. For either value obtained the magnitude is fairly small compared with other values reported for the general formation of rare earth complex by inorganic ligands. But it seems rather reasonable when considering the process as none or part of the hydrated water molecules in the primary sphere are released during the formation of extractable species. For the system of 0.3N HCl-0.2M $NaClO_4$ the tendency corresponds to the system of 0.2N HCl but the case of 0.3N HCl-0.2M NaCl it corresponds to the system of 0.3N HCl. These results can be explained as follows; perchlorate ion is relatively weak complexing agents as same

Table 5. Temperature Dependency of D of Lu for various Extraction Systems.

| Ext. system °C | $7.60 \times 10^{-2}M$ HDEHP -0.2N HCl (I) | $7.60 \times 10^{-2}M$ HDEHP -0.3N HCl (II) | $1.52 \times 10^{-1}M$ HDEHP -(0.3N HCl-0.2M $NaClO_4$) (III) | $1.52 \times 10^{-1}M$ HDEHP -(0.3N HCl-0.2M NaCl) (IV) |
|-------------------|--|---|--|---|
| 15 | — | 2.1 | 14.1 | 4.1 |
| 20 | 9.2 | 2.3 | 12.8 | 6.6 |
| 25 | 8.5 | 2.5 | 12.5 | 8.5 |
| 35 | 7.2 | 2.6 | 10.9 | 8.9 |
| 45 | 5.4 | — | 8.9 | — |

Table 6. *D* value of Lu at 20°C and 35°C for various aqueous systems.

| Exp. No. | [Aqueous phase | | | <i>D</i> | | HDEHP(M) in Toluene |
|----------|----------------|------------------------|---------|----------|-------|-----------------------|
| | HCl (M) | NaClO ₄ (M) | NaCl(M) | 20°C | 35°C | |
| 1. | 0.3 | 0.2 | 0 | 15.25 | 11.43 | 1.52×10 ⁻¹ |
| 2. | 0.3 | 0.17 | 0.03 | 13.80 | 10.13 | // |
| 3. | 0.3 | 0.13 | 0.07 | 11.39 | 9.81 | // |
| 4. | 0.3 | 0.1 | 0.1 | 9.39 | 9.44 | // |
| 5. | 0.3 | 0.07 | 0.13 | 9.11 | 9.40 | // |
| 6. | 0.3 | 0.03 | 0.17 | 7.34 | 9.36 | // |
| 7. | 0.3 | 0 | 0.2 | 6.56 | 9.01 | // |
| 8. | 0.1 | 0.1 | 0.3 | 3.20 | 2.38 | 4.56×10 ⁻² |
| 9. | 0.1 | 0.2 | 0.2 | 3.15 | 2.41 | 4.56×10 ⁻² |
| 10. | 0.2 | 0 | 0 | 9.27 | 7.06 | 7.60×10 ⁻² |
| 11. | 0.3 | 0 | 0 | 19.26 | 20.05 | 1.52×10 ⁻¹ |
| 12. | 0.4 | 0 | 0 | 12.11 | 13.19 | 2.28×10 ⁻¹ |

as nitrate ion and, in this system, the species formed in aqueous solution are mainly hydrated ion pair or outer sphere complex but for the system of 0.3N HCl-0.2M NaCl the species formed in aqueous phase may be a mixture of inner and outer sphere complex. According to such approach the results on Fig. 1. can be explained without difficulty.

This tendency can be seen again on the Table 6 which shows the *D* value at 20°C and 35°C for various aqueous composition of HCl, NaClO₄ and NaCl. The decreasing tendency of *D* value is changed to increasing tendency at Exp. No.4 which condition is 0.3N HCl-0.1M NaClO₄-0.1M NaCl and henceafter the same tendency is kept up to Exp. No. 7.

Conclusions

The observed different temperature dependencies between the lighter and heavier rare earth elements can be assigned as the difference in the ability of the formation of inner coordination complex with bulky HDEHP molecules. NO₃⁻ and ClO₄⁻ cannot

enter the inner sphere of the heavier rare earth cations by replacing coordinated water molecules in that sphere but SO₄⁼ and Cl⁻ would be able to form inner coordinated complex at higher concentration of the anions. Large HDEHP molecule would be able to form inner sphere complex with lighter lanthanons partially but it may be difficult for the heavier lanthanons. Thus, it is tentatively assumed that the extractable species in the organica phsse contains more hydrated water molecules in the primary shell of the heavier rare earth cations than the lighter rare earth cations This work should have more quantitative data to confirm such model and further work is under progressing.

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