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WITH 2,2,6,6-TETRAMETHYL 3,5-HEPTANEDIONE.

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SOLVENT EXTRACTION OF SOME LANTHANIDES WITH

2,2,6,6-TETRAMETHYL 3,5-HEPTANEDIONE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Henry Wisner Parlett, B.A., M. Sc.

* * * * *

The Ohio State University
1967

Approved by

A handwritten signature in cursive script, reading "Thomas R. Sweet", is written over a horizontal line.

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PREFACE

Recently, it has been demonstrated that the dipivaloyl methane (2,2,6,6-tetramethyl 3,5-heptanedione) chelates of the lanthanide elements are volatile and can be separated by gas chromatography. This study was undertaken to determine the conditions under which the lanthanide elements will successfully undergo liquid-liquid extraction with this ligand and to determine the formation constants of these chelates by solvent extraction techniques.

ACKNOWLEDGEMENTS

I wish to thank Dr. Thomas R. Sweet, my adviser, for his patience, advice and cooperation throughout this work. I also wish to acknowledge the cooperation of Dr. M.L. Pool, Physics Department, The Ohio State University, and his Gamma Spectroscopy Group for the use of their Radiation Instrument Development Laboratory Model 34-12B 400 channel analyzer and their low background cave. Without their cooperation, I would not have been able to use radio-isotopes in this study because of the low gamma energies of many of the lanthanide isotopes.

I am extremely grateful to the United States Air Force through its Air Force Institute of Technology, Air University, for this assignment to The Ohio State University for the purpose of working for this degree.

Above all, I am extremely and sincerely grateful for the love, patience, calmness and help of my wife Betty and children, Jim and Mary. Without their uncomplaining cooperation and sacrifice during this period, I would never have succeeded in this endeavor.

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CHAPTER I

HISTORICAL REVIEW

The extraction of metal ions from aqueous solution into an organic phase requires the use of a substance which will combine with the metal ion to form a neutral species. The first examples of such compounds were those in which the extractable species were formed by the association of ions. Among these was Peligot's discovery in 1842 that ether would extract uranium (IV) from nitric acid solution.¹ The first record of an extraction procedure used in analysis was described by Rothe.² This is the now classic extraction of ferric chloride from aqueous hydrochloric acid solutions from ether. Since this time, numerous ion association extraction systems have been described. Morrison and Freiser tabulated extraction data for many of these systems,³ and up-dated this information with reviews in Analytical Chemistry.⁴

The extraction of a metal ion in the form of a neutral chelate compound from an aqueous solution into an organic phase containing

¹Peligot, E., Anal. Chem. Phys., (3) 5 1 (1842).

²Rothe, J.W., Chem. News, 66 182 (1892).

³Morrison, G.W. and Freiser, H., "Solvent Extraction in Analytical Chemistry" (New York: John Wiley and Sons, 1957), Chap. 11.

⁴Morrison, G.W. and Freiser, H., Anal. Chem., 38 131R (1966); 36 93R (1964); 30 632 (1958).

a chelating agent was first done by Cazeneuve⁵ in 1900. He extracted chromium from an aqueous solution into benzene containing 1,5 diphenylcarbohydrazine. This work generated little interest and investigations of the phenomenon were not continued until several decades later when Feigl and Lederer⁶ used the method to purify various metal 1,5 diphenylcarbohydrazides. Since that time, the solvent extraction of metal chelates has grown into a distinct field of endeavor.

Unlike ion association complexes, for which the chemical equilibria are often quite complicated, the reactions of cations with organic chelating agents to give neutral and less hydrophilic species can usually be described by relatively simple equations. A number of other organic chelating agents such as cupferron and 8-hydroxy quinoline soon followed dithizone as reagents for the extraction of metal ions. Stary listed about fifty chelating agents which have been used for solvent extraction.⁷ In addition, the conditions for the extraction of various metal ions with these reagents are described in his book.

Among the various chelating agents used in solvent extraction, few have been more widely used than β -diketones. From 1948 to the present, numerous extraction studies have been performed using acetylacetone and thenoyltrifluoroacetone. Extraction data for several β -diketones have been collected and summarized in a table

⁵Cazeneuve, P., Compt. Rend., 131 346 (1900).

⁶Feigl, F. and Lederer, F.L., Monatsh., 45 116 (1924).

⁷Stary, J., "The Solvent Extraction of Metal Chelates", (New York: Pergamon Press, 1964), Appendix.

in Stary's book. Many other β -diketones such as benzoylacetone and dibenzoylmethane have been used.⁸ Recently dipivaloyl methane has been used to form chelates of lanthanides⁹ and several other metals.¹⁰ Khomenko and Kuznetzova¹¹ recently synthesized tris-dibenzoylmethanato complexes of some of the lanthanides.

Solvent extraction of the lanthanides has largely involved the use of tri-n-butyl phosphate and phosphoric acid esters such as di(2-ethylhexyl)phosphoric acid.¹² As is characteristic of all techniques of separation, no known reagent can give clear-cut separations between adjacent lanthanides, unless, as is true in only a limited number of cases, these elements can exist in two different oxidation states. Most organo-phosphorous extractant systems have separation factors between adjacent lanthanides on the order of 1.5 - 2.5. As pointed out by Peppard and Mason,¹³ a separation factor in the neighborhood of 2 is sufficiently large to purify one lanthanide from another provided that countercurrent operation of a large number of stages is readily accomplished. This was

⁸Stary, J. and Hladky, E., Anal. Chem. Acta, 28 227 (1963).

⁹Eisentraut, K. and Sievers, R.E., J. Am. Chem. Soc., 87 5254 (1965).

¹⁰Hammond, G.S., Nonhebel, D.C. and Wu, C.S., Inorg. Chem., 2 73 (1963).

¹¹Khomenko, V.S. and Kuznetzova, V.V., Doklady Akad. Nauk. Belorussk. S.S.R., 9 610 (1963).

¹²Moeller, T., et al., Chemical Reviews, 65(1) 29 (1965).

¹³Peppard, D.F. and Mason, G.W., "Rare Earth Research", ed. Eugene V. Kleber (New York: MacMillan Co., 1961), p. 37.

used for the purification of a gadolinium fraction in the kilogram range and the separation of promethium from its neighboring rare earth radioactive fission products.¹⁴

With the exception of acetylacetone and thenoyl trifluoroacetone, little work has been done with beta diketones and the lanthanides.¹⁵

Most procedures used in chelate solvent extraction systems have involved the organic chelating agent dissolved in an organic solvent such as benzene, carbon tetrachloride, chloroform, etc. Recently there have been publications in which the organic chelating agent is used both as the chelating agent and the solvent. The first one was the use of acetylacetone by Steinbach and Freiser.¹⁶ Stary¹⁷ reported several cases in which acetylacetone was used pure in an attempt to extract some of the lanthanides. Brown, Steinbach and Wagner¹⁸ studied the distribution of eight lanthanides and yttrium using acetylacetone as a chelating solvent. Very recently, Schweitzer and VanWillis¹⁹ used 7-methyl-2,4-octanedione and 1,1,1-trifluoro-7-methyl-2,4-octanedione as chelating solvents in the extraction of nine metals. As

¹⁴Ibid.

¹⁵Moeller, T. et al., Chemical Reviews, 65(1) 29 (1965).

¹⁶Steinbach, J.F. and Freiser, H., Anal. Chem., 26(6) 881 (1953).

¹⁷Stary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p. 55.

¹⁸Brown, W.B., Steinbach, J.F. and Wagner, W.F., J. Inorg. and Nucl. Chem., 13 119 (1960).

¹⁹Schweitzer, G.K. and VanWillis, W., Anal. Chim. Acta, 36 77-89 (1966).

will be shown later, the large concentration of the chelating agent in the organic phase enhances extraction at lower pH values and also the similarity of the metal chelate and the chelating solvent probably leads to larger solubilities of the chelate in the solvent.

Recently, Sievers and Eisentraut²⁰ have shown that some inorganic chelates can be separated by gas chromatographic techniques.²¹ Morie and Sweet²² have developed a procedure for the separation of aluminum and iron by solvent extraction and gas chromatography.

In addition to these practical applications of solvent extraction, the technique has been used for some time to determine formation constants of the chelates. The first record in which solvent extraction was used to determine stability constants precedes the better known potentiometric work of Bjerrum.²³

In a classic investigation of the complex formation between Hg^{+2} and X^- ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) Morse²⁴ made use of the fact that HgX_2 molecules are soluble in toluene. From the distribution of mercury between toluene and water as a function of X^- , he

²⁰Eisentraut, K. and Sievers, R.E., J. Am. Chem. Soc., 87 5254 (1965).

²¹Sievers, R.E. and Mosher, R.W., "Gas Chromatography of Metal Chelates" (New York: Pergamon Press, 1965).

²²Morie, G.P. and Sweet, T.R., Anal. Chim. Acta, 34 314 (1966).

²³Bjerrum, J., "Metal Amine Formation in Aqueous Solution", diss., Copenhagen, 1941.

²⁴Morse, H., Z. Physik. Chem., 41 709 (1902).

calculated the concentration of HgX^+ and HgX_2 and subsequently the constant for the formation of HgX^+ .

Connick and McVey²⁵ studied the nature of the zirconium (IV) species which exists in aqueous solution by means of two phase distribution equilibria. Using a benzene-thenoyl trifluoroacetone solution, they deduced the formulas and stabilities of the zirconium species in the aqueous phase from the variation of the distribution ratio as a function of the aqueous solution composition.

It was not until 1950 that the stability of a metal chelate was determined using solvent extraction. In this year, Rydberg developed equations for the thorium acetylacetone system and calculated step-wise stability constants for all four species.²⁶ This study was quite comprehensive and only two assumptions were made: (1) no charged species are present in the organic phase and (2) no hydrolysis of the metal ion occurs. Both of these assumptions are valid for this particular system. In the following years, Rydberg made several studies in which additional equilibria, including hydrolysis, were included in the final equation.^{27,28}

Krishen and Freiser²⁹ calculated the stability constants for acetylacetone complexes of aluminum, beryllium, copper, gallium,

²⁵Connick, R.E. and McVey, W.H., J. Am. Chem. Soc., 71, 3182 (1949)..

²⁶Rydberg, J., Acta Chem. Scand., 4 1503 (1950).

²⁷Rydberg, J., Arkiv. Kemi., 8 101 (1955).

²⁸Rydberg, J., Rec. Trav. Chim., 75 737 (1956).

²⁹Krishen, A. and Freiser, H., Anal. Chem., 37 923 (1959).

hafnium and other metals using extraction data. They used very high reagent concentrations and were therefore able to neglect hydrolysis of the metal ions. In general, the results obtained in their study agree well with constants that were calculated from potentiometric data.

Recently, Morie³⁰ determined the formation constants of the trifluoroacetylacetone complexes of aluminum, gallium, indium and iron. Panova et al.³¹ have used this technique to determine the overall formation constants of the yttrium 3-hydroxy quinolinate chelate. Rossotti and Rossotti³² have summarized several techniques for the calculation of these constants.

³⁰Morie, G.P., Ph.D. Dissertation, The Ohio State University, 1966, p. 132.

³¹Panova, M.G., Levin, V.I. and Brezhneva, N.E., Radiochemistry, USSR, Vol. II, No. 2, (1960), p. 209.

³²Rossotti, F.J.C. and Rossotti, H., "Determination of Stability Constants" (New York: McGraw Hill, 1961), Chap. 5 & 10.

CHAPTER II

EXPERIMENTAL

I APPARATUS

Activity measurements of all gamma emitting isotopes were made using a Radiation Instrument Development Laboratory Model 34-12B 400 channel analyzer. The analyzer was connected to a 3" x 3" Harshaw NaI(Tl) Integral scintillation crystal 12S12 located in a lead cave. Data print-out was by IBM automatic typewriter. This arrangement for the measurement of gamma radiation is commonly used. The gamma rays are absorbed by the crystal and produce scintillations which are detected by a photomultiplier tube, amplified and recorded in a memory unit. The analyzer is equipped with a live time clock so no corrections for coincident losses due to high count rate need to be made. The instrument can be calibrated for different energy ranges. The energy range used for 200 channels and energy peaks for each isotope used are given in Table 1.

Liquid samples were counted in two dram screw cap vials. Geometry was maintained constant by means of a positioning guide on top of the crystal. The crystal was covered with 253 mg/cm² Al equivalent as part of the normal protective covering of the crystal.

The use of the RIDL 400 channel analyzer allowed purity checks on each isotope.

TABLE 1
Counting Conditions and Properties of Radioisotopes Used

Isotope	Half Life	Energies of Peaks Used to Determine Dist. Ratio	Energy Range for 200 Channels
^{141}Ce	32 days	145 kev	400 kev
^{142}Pr	19 hour	*	*
^{153}Sm	47 hour	43, 102 & 146 kev	400 kev
$^{152-154}\text{Eu}$	152 - 13 yr. 154 - 16 yr.	40, 135 & 395 kev	400 kev
^{153}Gd	236 days	43, 102 & 146 kev	400 kev
^{160}Tb	73 days	47, 85 & 338 kev	400 kev

* Sample counted in a 5" x 5" well crystal using an integral scaler.

A Beckman Model G pH meter equipped with a Thomas 4858-L60 combination glass, silver-silver chloride electrode was used for pH measurements.

A Burrell wrist action shaker was used to agitate the solutions during batch equilibrium studies. Samples were shaken in 30 ml duraglass screw cap bottles which had a polyethylene cone sealing device in the cap.

Spectrophotometric measurements were made with a Bausch and Lomb Spectronic 505 Recording Spectrophotometer.

All isotopes used were > 98% radiochemically pure from the

supplier and no extraneous peaks were observed in the spectra during the time of the experiments. They were supplied by Oak Ridge National Laboratory, Nuclear Chicago, or Nuclear Science and Engineering Company.

II REAGENTS

All reagents used in this investigation were analytical reagent grade unless otherwise specified. Double-distilled demineralized water containing less than one tenth part per million of impurities was used.

Dipivaloyl Methane

Dipivaloyl methane (DPM), 2,2,6,6 tetramethyl 3,5 heptanedione, was received from Pierce Chemical Co. Its purity was checked by distillation (boiling point 104-105° C. @ 35 mm),¹ by refractive index, gas chromatography, nuclear magnetic resonance and infra red spectra.

The refractive index was reported by Linn and Hauser² as 1.4572 at 25° C. for the sodium D line. An investigator in this laboratory using distilled DPM showed the refractive index to be 1.4572 ± 0.0002 at 25° C.,³ in excellent agreement with the value

¹Literature values reported were: 94.0-94.5° C. @ 20 mm., Guter, G.A. and Hammond, G.S., J. Am. Chem. Soc., 78 5166 (1956); 93-94° C. @ 35 mm, Man, E.H., Swamer, F.W. and Hauser, C.R., J. Am. Chem. Soc., 73 901 (1951); 93-94° C. @ 35 mm, Hammond, G.S., Nonhebel, D.C. and Wu, C.S., Inorg. Chem., 2 73-76 (1963); 89-89.5° C. @ 18 mm, Linn, B.O. and Hauser, C.R., J. Am. Chem. Soc., 78 6066 (1956).

²Linn, B.O. and Hauser, C.R., J. Am. Chem. Soc., 78 6066 (1956).

³Hobstetter, L.E., Private Communication.

reported. The refractive index change with temperature change was also determined in this laboratory as $-0.00047/^{\circ}\text{C.}$ in the range $15-25^{\circ}\text{C.}$

Gas chromatography was performed by injecting 10 microliter samples into a Chromosorb R solid support with 20% Carbowax 20M liquid phase and column temperatures from 125°C. to 200°C. A single peak was obtained with retention time of 5.3 minutes at 50 ml./minute He carrier gas flow rate at column temperature of 150°C.

Nuclear magnetic proton resonance spectra of the neat reagent were run on a Varion A-60. Peaks were found at the following chemical shifts (ppm with reference to internal tetramethyl silane): 1.15, 2.21, 3.68, 5.75. These are in agreement with those determined by Sievers who also determined that DPM exists as approximately 98% enol and 2% keto form in the pure liquid.⁴ This confirms the work of Hammond et al.⁵ who determined that DPM is essentially 100% enolic from the infra red spectra.

In addition to the above tests, a portion of the DPM was put through another purification procedure and the ligand was regenerated and distilled. No difference was detected in any of the tests between samples as received from Pierce Chemical Co., samples after distillation and samples after repurification. The

⁴Sievers, R.E., Private Communication.

⁵Hammond, G.S., Bordium, W.G. and Guter, G.A., J. Am. Chem. Soc., 81 4682 (1959).

purification procedure used was based on that of Hammond et al.⁶ and consisted of precipitating and recrystallizing the copper chelate and then regenerating the ligand by dissolving the chelate in a 10% HCl solution and extracting the ligand into ether and distilling the ligand.

On the basis of the above purity tests, the only purification that was performed on the reagent as received from the manufacturer was a simple distillation at 35 mm pressure using a 6" Vigreux column.

The molar absorptivity of an aqueous solution of DPM was reported to be 0.18×10^4 liter mole⁻¹ cm⁻¹ by Hammond et al.⁷ and 0.19×10^4 liter mole⁻¹ cm⁻¹ by Hammond, Nonhebel and Wu⁸ at 278 mμ. Aqueous solutions of DPM were prepared with concentrations ranging from 1×10^{-4} M to 5.5×10^{-4} M and the ultra violet spectra determined. A single absorption peak was obtained at 278 mμ, in agreement with that reported by Hammond et al.⁹ and to be expected for a carbonyl chromophore.¹⁰ The solutions were at pH < 6.0 at which the reagent exists essentially in the un-ionized form.

⁶Hammond, G.S., Nonhebel, D.C. and Wu, C.S., Inorg. Chem., 2 73-76 (1963).

⁷Hammond, G.S., Bordium, W.G. and Guter, G.A., J. Am. Chem. Soc., 81 4682 (1959).

⁸Hammond, G.S., Nonhebel, D.C. and Wu, C.S., Inorg. Chem., 2 73 (1963).

⁹Hammond, G.S., Bordium, W.G. and Guter, G.A., J. Am. Chem. Soc., 81 4682 (1959).

¹⁰Rao, C.N.R., "Ultra-Violet and Visible Spectroscopy" (London: Butterworth's, 1961), p. 17.

The molar absorptivity of un-ionized DPM at 278 m μ was determined to be 0.195×10^4 liters mole⁻¹ cm⁻¹ (standard deviation of the mean was 0.4%) at 25° C. This value is based on a total of 48 determinations on 14 solutions of different strengths.

The density of DPM was also determined in this laboratory to be 0.898 g/ml at 25° C.¹¹

Dipivaloyl methane behaves as a very weak monobasic acid in aqueous solution where it exists essentially in the keto form. Hammond et al.¹² report the enol/keto ratio to be 0.16 in aqueous solution. The pK_a was reported as 11.77 by Guter and Hammond¹³ as determined spectrophotometrically in a 0.01 ionic strength. Porell¹⁴ of this laboratory determined the pK_a of DPM in a 0.1 ionic strength aqueous solution. He used a spectrophotometric procedure and determined the pK_a to be 11.76.

Using this value, the solubility of DPM at 24° C. as a function of pH was determined by shaking 5-ml portions of DPM with 10-ml portions of 0.1 M (C₂H₅)₄NC10₄ and performing spectrophotometric measurements on the aqueous solution.

The absorbance and equilibrium pH were measured and the

¹¹Hobstetter, L.E., Private Communication.

¹²Hammond, G.S., Bordium, W.G. and Guter, G.A., J. Am. Chem. Soc., 81 4682 (1959).

¹³Guter, G.A. and Hammond, G.S., J. Am. Chem. Soc., 78 5166 (1956).

¹⁴Porell, A.L., Private Communication.

solubility obtained by the following equations if the peak of the absorbance curve was obtained at 278 m μ .

$$A_{278} = \epsilon_{HR_{278}} [HR] \quad \text{using 1 cm cells}$$

The solubility was then equal to concentration of HR as essentially all the dipivaloyl methane was in the un-ionized form. If the peak of the absorbance curve was not at 278 m μ , then the solubility was obtained by measuring the absorbance at 295 m μ , having already determined the molar absorptivity of the acid and ionized forms at that wavelength. The ionized form of DPM has a single absorption peak at a wavelength of 295 m μ . The following equations were used:

$$A_{295} = \epsilon_{HR_{295}} [HR] + \epsilon_{R_{295}} [R] \quad (1 \text{ cm cells})$$

$$HR = \frac{[H][R]}{K_a}$$

$$= \left(\epsilon_{HR_{295}} \left(\frac{H}{K_a} \right) + \epsilon_{R_{295}} \right) [R]$$

$$\text{Sol} = [HR] + [R]$$

A plot of the solubility is shown in Figure 1. Saturation was attained in 15 minutes as evidenced by a time study up to 1½ hours shaking time.

Rare Earth Solutions

Rare earth nitrates were obtained from Lindsay Division of American Potash and Chemical Company in purities 99.9% or greater.

Stock solutions of about 0.1 M M⁺³ concentration were prepared and standardized by an EDTA titration using Xylenol

FIGURE 1

Solubility of
2,2,6,6 Tetramethyl 3,5 Heptanedione
(DPM)
in 0.1 M $(C_2H_5)_4NClO_4$

Orange indicator¹⁵ and by a gravimetric procedure in which an aliquot of the rare earth solution (to which some saturated oxalic acid was added) was evaporated in a weighed crucible and then ignited for one hour at 1000° C. to form the oxide. Agreement between these two methods was within less than 1%.

Dilutions to the desired strength were then made from the stock solutions. The ionic strength of the dilute solutions was adjusted to 0.1 with $(C_2H_5)_4NClO_4$.

The stock solutions were checked for purity by running their absorption spectra in the range 220 mμ - 800 mμ. The absorption spectra were checked against the spectra shown in Kolthoff and Elving, "Treatise on Analytical Chemistry".¹⁶

III PROCEDURE

Solutions of the individual lanthanides were prepared in the desired concentrations by diluting the stock solutions. All solutions were adjusted to 0.1 ionic strength with $(C_2H_5)_4NClO_4$. Radioactive tracers were added at the time of dilution. All work was performed at $24 \pm 1^\circ$ C.

Initial experimental work was performed by transferring 10.0 ml of a 2.5×10^{-3} M metal solution into a 30-ml bottle and adjusting the pH to an initial value by means of $(C_2H_5)_4NOH$ and $HClO_4$. A 5.0-ml portion of the reagent DPM in benzene was then

¹⁵Kolthoff, I.M. and Elving, P.S. (ed.), "Treatise on Analytical Chemistry" (New York: John Wiley and Sons, Inc., Interscience Publishers, 1963), Part II, Vol. 8, p. 57.

¹⁶Ibid., p. 103 ff.

added and the bottle was shaken on the Burrell shaker for the desired length of time. These initial preliminary experiments did not achieve essentially 100% extraction at any pH value unless a 1.5 M or higher solution of DPM in benzene was used as the organic phase. It was decided, since pure DPM is 4.9 M, to do extractions with the reagent as the chelating solvent, i.e., as both the chelating agent and the solvent for the chelate. With this exception, the same procedure was followed and under the proper conditions of pH, essentially 100% extraction occurred. In order to attain this, it was necessary for the initial pH to be greater than 8. This meant that the metal hydroxide had precipitated. Thus, whenever the element of interest was initially in the aqueous phase, there was a solid phase involved in the reaction. In addition, it was found that the distribution ratio values (D)

$$D = \frac{\text{total conc. of metal in organic phase}}{\text{total conc. of metal in aqueous phase}}$$

were highly scattered and irreproducible at high D values. It was not possible to adequately determine the shape of the curve of log D vs pH which is needed for calculation of the formation constants. It was also found that when an aqueous phase aliquot was taken for counting, different counts would be obtained depending upon the degree of agitation of the bottle during normal handling. Since no precipitate was visible, this was attributed to the formation of a local irreversible precipitate on the colloidal level during the pH adjustment.

To avoid this problem, determinations were made with the chelate initially in the organic phase, i.e., in pure DPM. Since greater than 99% was extracted into the organic phase from the

aqueous phase with 1/2 hour shaking, the chelate was first formed and extracted as stated above. This formed the stock solution that was used for the determination of the distribution ratio. Five ml of this solution was equilibrated with 10.0 ml of 0.1 M $(C_2H_5)_4NClO_4$ which had been previously adjusted to the desired pH. Data were found to be reproducible and not as scattered as with the forward extraction method. In addition, this procedure has the advantage that a constant volume ratio may be maintained between the two phases which is not possible in the forward system, due to the formation of the hydroxide precipitate. Also the organic phase is already saturated with aqueous 0.1 M $(C_2H_5)_4NClO_4$ solution and there is no volume change. The volume change due to the solubility of DPM in the aqueous phase is negligible throughout most of the range and is only about 0.5% at pH 12.5.

Two milliliter aliquots of each phase were taken for counting. Since many samples had low count rates (less than 100 counts per minute), extreme precautions were taken to avoid accidental contamination of the sample vials and to keep the background as low as possible. The crystal was covered by a large piece of parafilm which was changed weekly. The glass sample vials were washed after filling and then placed in a new polyethylene vial which was handled at all times with disposable plastic gloves.

The organic phases of DPM and chelate were periodically collected and the DPM was recovered by distillation at 35 mm pressure. The chelate remained behind in the distilling flask. The distillate was collected, stirred for at least three hours with a 10% H_2SO_4 or HCl solution and then was redistilled. Its

purity was checked by means of refractive index measurements and by counting an aliquot on the 400 channel analyzer. If pure, the DPM was reused.

CHAPTER III

MATHEMATICAL DEVELOPMENT

Solvent extraction is based on the distribution of a solute between two immiscible phases. For this case, the classical phase rule of Gibbs can be applied:

$$P + F = C + 2 \quad (3-1)$$

where P is the number of phases, F the number of degrees of freedom and C the number of components. According to this equation, a system consisting of two immiscible solvents and one solute distributed between them has one degree of freedom at constant temperature and pressure. Thus, if the concentration of the solute in one phase is constant, the concentration of the solute in the other phase is also fixed. The constant giving the concentration ratio of the solute between both phases at equilibrium is called the partition coefficient, P , which can be expressed by the following equation:

$$P = c_{\text{org}} / c \quad (3-2)$$

where c_{org} and c denote the concentration of the distributed compound in the organic and aqueous phases respectively. Thus, it follows that the partition coefficient does not depend on the total solute concentration or on the actual phase volumes. The distribution law is only valid if the solute is in the identical chemical form in both phases.

The partition coefficient, P , of a compound is approximately equal to the ratio of its solubilities in the organic and aqueous phases.¹ Thus only such compounds can be usefully extracted as are only slightly soluble in water but readily soluble in organic solvents. In essentially all metal extraction systems, some or all of the solvated water molecules must be removed to obtain a species extractable by organic solvents. This species must, however, be uncharged because of the low dielectric constant of the organic solvents that are generally used in extraction procedures.

In order to write an equation which can be used to calculate successive stability constants, it is necessary to list all of the equilibria involved. The basic relationship involves the distribution ratio, D , defined as the ratio of the total metal concentration in the organic phase to that in the aqueous phase:

$$D = \frac{[M]_{org}}{[M]_{aq}} \quad (3-3)$$

The relationship refers to organic and aqueous phase activities but concentrations may be substituted for activities without too much error, particularly where there is little change in ionic strength or in the organic solvent and this substitution will be assumed hereafter. Also organic phase concentrations will be subscripted with an "o" while aqueous phase concentrations will be unsubscripted. In addition, charges will be omitted for simplicity.

A system designed for solvent extraction of a metal chelate ordinarily consists of two phases, one of which is water and the

¹Stary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p. 2.

other an immiscible organic solvent. The organic solvent before contact ordinarily contains a known concentration of a monobasic bidentate chelating agent, HR, and it may contain an adducting agent, B, and it usually is presaturated with water. The aqueous phase before contact contains the metal ion M. In addition, this may contain an aqueous complexing agent, X, (such as thiocyanate, chloride, etc.). It will also have given concentrations of hydrogen and hydroxide ion and it may be made up to a given ionic strength with inert ions such as Na^+ , ClO_4^- or, as in this series of experiments, $(\text{C}_2\text{H}_5)_4\text{N}^+$ and ClO_4^- . It is usually presaturated with organic phase, particularly if the organic phase has an appreciable solubility in water.

When the phases are equilibrated, a number of reactions may occur. The molecules of B and HR may partition into the aqueous phase, where HR will ionize to some extent depending upon the H concentration. The metal ion may combine with the molecules B, HR, S (organic solvent) and H_2O and with the ions X, CH and R to form complexes. Any neutral species resulting from these combinations may then partition into the organic phase.

Thus equation 3-3 may be written as follows:

$$D = \frac{\sum_{M R A B X H W S} \left[M_i R_j (\text{HR})_k B_l X_n (\text{OH})_p (\text{H}_2\text{O})_t S_v \right]_0}{\sum_{i j k l n p t v} \left[M_i R_j (\text{HR})_k B_l X_n (\text{CH})_p (\text{H}_2\text{O})_t S_v \right]} \quad (3-4)$$

In this study there were no adducting agents, B, or complexing agents, X, and since the system uses the chelating agent, HR, as a chelating solvent, S and HR can be combined.

Then the equation above may be simplified:

$$D = \frac{\sum_{M R A H W} [M_R R (HR)_A (OH)_H (H_2O)_W]_0}{\sum_{i j k p t} [M_i R_j (HR)_k (OH)_p (H_2O)_t]} \quad (3-5)$$

Since the concentrations of H_2O and the organic solvent are large in a particular system, they may be considered invariable and their values can be absorbed in the partition and formation constants to be developed later.

Equation 3-5 may be further simplified:

$$D = \frac{\sum_{M R H} [M_R R (OH)_H]_0}{\sum_{i j p} [M_i R_j (OH)_p]} \quad (3-6)$$

The denominator of equation 3-6 can be expanded as shown below to cover all possible species. As this study of the lanthanides involves a trivalent species and a monoprotic bidentate chelating agent, ER, it will be written in the specific terms involved:

$$D = \frac{\sum_{M R H} [M_R R (OH)_H]_0}{[M] + [MR] + [MR_2] + [MR_3] + [MR_4] + [MOH] + [M(OH)_2] + [M(OH)_3] + [MRCH] + [MR_2OH] + [MR_3OH] + [MR_3(OH)_2] + [MR_2(OH)_2] + [MR_2(OH)_3] + [MR_4CH] + [MR(OH)_2] + [MR(OH)_3] + [MR(OH)_4]} \quad (3-7)$$

Since $M(OH)_3$ is insoluble for all the lanthanides ($K_{sp} = \sim 10^{-22}$) and as there was no evidence of a hydroxide precipitate existing at equilibrium, the $M(OH)_3$ can be dropped. A series of formation

constants can now be written involving the formation of these aqueous species, as represented by the following general equations:

This work deals only with trivalent lanthanides, univalent chelate and hydroxide ion and it can be seen from equation 3-7 that only three neutral species may be formed, which are therefore capable of being extracted into the organic phase. Substituting equations of the type represented by equations 3-8 and 3-9 in equation 3-7 and factoring out M^3 from each term:

$$D = \frac{[\text{MR}_3]_o + [\text{MR}_2\text{OH}]_o + [\text{MR}(\text{OH})_2]_o}{[\text{M}](1 + \beta_{jo}[\text{R}]^j + \beta_{jp}[\text{R}]^j[\text{OH}]^p + \beta_{op}[\text{OH}]^p)} \quad (3-10)$$

As pointed out by Stary² the partition coefficient of hydroxy-complexes between the organic solvent (especially those with low dielectric constants) and the aqueous phase will, in practically all cases, be low in comparison with the partition coefficient of the neutral metal chelate MR_3 . Thus the concentration of MR_2OH would be expected to be low in the organic phase compared to the

²Ibid., p. 12.

concentration of MR_3 , and that of $MR(OH)_2$ would be expected to be even lower. Since a chelating solvent is involved here, it is easy to see the structural similarity between HR , MR_3 , MR_2OH and $MR(OH)_2$. Since like tends to dissolve like, MR_2OH might be only slightly less soluble than MR_3 , and $MR(OH)_2$ probably much less soluble. However, Wagner and his coworkers^{3,4,5} found it desirable to use excess acetylacetone in the organic phase to repress hydrolysis and also to use an open vial of acetylacetone in a desiccator while preparing lanthanide acetylacetonates to repress hydrolysis. They also showed that the addition of acetylacetone to solid monobasic lanthanide chelate, $LnCH(C_5H_7O_2)_2$, converted it to the monohydrated compound, $Ln(C_5H_7O_2)_3 \cdot H_2O$.

In addition, as pointed out by Guter and Hammond,⁶ it was necessary for them to use an excess of chelating agent to eliminate hydrolysis in the determination of formation constants of metal chelates by Bjerrum's method. Thus it seems that the presence of a large excess of chelating agent appears to drive the reaction to the fully chelated neutral form. In addition, Eisentraut and Sievers⁷ have shown that the lanthanide dipivaloyl methane chelates exist as stable anhydrous species. In view of the above and the

³Brown, W.B., Pope, G.W., Steinbach, J.F. and Wagner, W.F., J. Inorg. Nucl. Chem., 25 429 (1963).

⁴Pope, G.W., Steinbach, J.F. and Wagner, W.F., J. Inorg. Nucl. Chem., 20 304 (1961).

⁵Wagner, W.F., Record Chem. Prog., 23(3) 155 (1962).

⁶Guter, G.A. and Hammond, G.S., J. Am. Chem. Soc., 81 4686 (1959).

⁷Eisentraut, K. and Sievers, R.E., J. Am. Chem. Soc., 87 5254 (1965).

work covered in Chapter IV, it appears reasonable that only MR_3 species exists in the organic phase (pure dipivaloyl methane) and accordingly, equation 3-10 can be amended to include only $[MR_3]_O$ in the numerator.

Substituting $[M^{+3}] = [MR_3]/\beta_{30}[R]^{-3}$ into equation 3-10 and defining the partition coefficient of the chelated species as

$$P_c = \frac{[MR_3]_O}{[MR_3]} \quad (3-11)$$

the following general equation is derived:

$$D = \frac{P_c \beta_{30} [R]^{-3}}{1 + \sum_{j=0}^j \sum_{p=0}^p \beta_{jp} [R]^{-j} [OH]^{-p}} \quad (3-12)$$

Equation 3-12 is thus the general basic equation showing the relationship between $[R^-]$, D and $[OH^-]$. Since a saturated solution of the chelating agent is attained, and the metal ion concentration is low compared to the solubility, one can calculate $[R^-]$ from pH and solubility data, knowing the dissociation constant K_a . If the chelating agent is dissolved in an organic solvent, one has to determine the partition coefficient of the reagent between the two phases as a function of pH and the dissociation constant K_a .

CHAPTER IV

RESULTS AND DISCUSSION

I Time and Concentration Study

Due to the chemical similarity of the lanthanides, europium was chosen to make a time and concentration study.

A time study is necessary to show that equilibrium has been attained between the two phases. If equilibrium is attained, a constant distribution ratio will be obtained at a particular pH. Thus, by determining the ratio as a function of time, it is possible to find the minimum time necessary to obtain equilibrium. In this study, the back extraction system was used starting with the chelated element in the organic phase. The results of the time study for europium are shown in Table 2. From the results, it appears that five hours is sufficient to attain equilibrium.

A lanthanide concentration study is necessary to examine the possibility of formation of polynuclear species in either the organic or aqueous phase. As pointed out by Schweitzer and VanWillis,¹ if $\log D$ is plotted against $\log$ metal ion concentration, a zero slope will be found in the region where polynuclear species

¹Schweitzer, G.K. and VanWillis, W., "Advances in Analytical Chemistry and Instrumentation" (New York: John Wiley and Sons, Inc., 1966), Vol. V, p. 173.

TABLE 2

Equilibrium Shaking Time Study

$M^{+3} = 2.5 \times 10^{-5}$ M in aqueous phase. Back extraction procedure*

Shaking Time	pH	Distribution Ratio
1 hour	6	34×10^4
	10 - 11	$\sim 5 \times 10^3$
	12	$\sim 5 \times 10^3$
2 hours	6	25×10^4
	10 - 11	$\sim 6 \times 10^3$
	12	$\sim 3.8 \times 10^3$
3 hours	6	18×10^4
	10 - 11	$\sim 7 \times 10^3$
	12	2.4×10^3
5 hours	6	15×10^4
	10 - 11	$\sim 7 \times 10^3$
	12	2.3×10^3
22 hours	6	15×10^4
	10 - 11	$\sim 6 \times 10^3$
	12	2.4×10^3
66 hours	10 - 11	$\sim 6 \times 10^4$

* The forward extraction system showed a gradual increase with D but equilibrium was not attained for 24 hours and the D values did not attain the same values as above.

do not exist. If polynuclear species are formed in the organic phase, a positive slope will be found whereas a negative slope will be found if polynuclear species are formed in the aqueous phase.

Theoretical plots are shown in Figure 2.

The effect of concentration on extraction of europium was made in both forward and back extraction systems. The results of the back extraction system used in this study are shown in Table 3.

TABLE 3

Concentration Study on Extraction of Eu^{+3}

Back Extraction Procedure

Shaking Time - 5 hours

Eu^{+3} Concentration	pH	D
2.5×10^{-3}	6	35
	10 - 11	$\sim 5.5 \times 10^4$
	12	3.4×10^3
2.5×10^{-4}	6	17
	10 - 11	$\sim 7 \times 10^4$
	12	2.4×10^3
2.5×10^{-5}	6	15
	10 - 11	$\sim 7 \times 10^4$
	12	2.3×10^3

The forward extraction system gave similar results but with lower and more scattered D values at the 9-12 pH range (see Chapter II). However, it did confirm the existence of mononuclear species at 10^{-4} and 10^{-5} M metal ion concentrations.

On the basis of the results in Tables 2 and 3 and considering the similarities between the individual lanthanides, it was determined that equilibrium for the back extraction system was attained

FIGURE 2

Theoretical Plot Showing Formation
of Polynuclear Species

- a = No polynuclear species in either phase.
- b = Polynuclear species in organic phase.
- c = Polynuclear species in aqueous phase.

in five hours and that only mononuclear species were extracted or existed in the aqueous phase at $< 10^{-4}$ M aqueous phase metal ions. Thus all lanthanides studied were shaken for five hours and initial metal ion aqueous phase metal concentrations of 2.5×10^{-5} M.

II Percent Extraction Studies

The final equation developed in Chapter III (equation 3-12) for the distribution ratio, D, can be simplified when certain conditions exist. If there is a region where hydrolysis does not occur and where the amount of neutral chelated species and intermediate species in the aqueous phase can be considered negligible compared to the free metal ion concentration, the equation can be simplified to:

$$D = \frac{P_c \beta_3 [R]^n}{1} \quad (4-1)$$

As R is a function of pH and the solubility of the reagent HR in the aqueous phase, equation 4-1 can be changed to

$$D = \frac{P_c \beta_3 K_a^n [HR]^n}{[H^+]^n} \quad (4-2)$$

Since the pH range where only free metal ion predominates is in the range where $[HR]_{aq}$ is a constant (see Chapter II on solubility of dipivaloyl methane), equation 4-2 may be written as

$$D = K^* [H^+]^{-n} \quad \text{where } K^* = P_c \beta_3 K_a^n [HR]^n \quad (4-3)$$

or

$$\log D = \log K^* - n \log [H^+] = \log K^* + n \text{ pH}$$

Thus a plot of $\log D$ vs pH will give a slope of $+3$ in the region where only hydrated trivalent metal ion predominates in the aqueous phase and no hydrolysis occurs. The distribution of the metal then is a function of pH alone.

From the definition of distribution ratio, D , an equation relating % E and D can be derived.

$$\text{Percent extraction} = \frac{\# \text{ moles metal species in org. phase} \times 100}{\text{total } \# \text{ moles of metal in both phases}} \quad (4-4)$$

$$\%E = \frac{[M]_{T_{org}} V_o (100)}{[M]_{T_{org}} V_o + [M]_{T_{aq}} V_{aq}} \quad (4-5)$$

Dividing numerator and denominator by $[M]_{T_{aq}} V_o$ and recalling that

$$D = \frac{[M]_{T_o}}{[M]_{T_{aq}}}$$

then

$$\%E = \frac{100 D}{D + \frac{V_{aq}}{V_o}} \quad (4-6)$$

where V_{aq} and V_o are the volume of aqueous and organic phases respectively.

Equation 4-6 can be rearranged to give

$$D = \frac{\% E}{100 - \% E} \left(\frac{V_{aq}}{V_o} \right) \quad (4-7)$$

Equations 4-3 and 4-7 can now be equated.

$$D = \frac{\% E}{100 - \% E} \left(\frac{V_{aq}}{V_o} \right) = K^* [H^+]^{-n} \quad (4-8)$$

$$\text{or } \log \% E - \log (100 - \% E) + \log \frac{V_{aq}}{V_o} = \log K^* + n \text{ pH} \quad (4-9)$$

Equation 4-9 represents a family of lines, if $\log \% E - \log (100 - \% E)$ is plotted against pH, with the position of each along the pH axis depending only on the magnitude of K^* and the volume ratio and the slope of each being 3 in the case of a tri-valent free metal ion. If $\% E$ is plotted vs pH, a family of symmetrical sigmoid curves results, the slope of which depends uniquely on n , i.e., on the charge of the ion, as shown below.

$$\ln \% E - \ln (100 - \% E) = K^* + 2.303 n \text{ pH}$$

$$\frac{dE}{E} - \left(\frac{1}{100 - E} \right) (-1) dE = 2.303 n \text{ pH}$$

$$\frac{dE}{d\text{pH}} = 2.303 n \frac{E(100 - E)}{100} \quad (4-10)$$

Naturally, in extractions where equation 4-9 is not strictly applicable, such as those in which hydrolysis of the metal occurs or in which intermediate chelate forms occur, the slope of the extraction curve cannot be expected to be proportional to the charge on the metal, n , but will be found to be significantly lower.

The pH value at which 50% extraction occurs has been designated as $\text{pH}_{\frac{1}{2}}$ and from equation 4-9, its value is

$$\begin{aligned} \log 50 - \log 50 + \log \frac{V_{aq}}{V_o} - \log K^* &= 3 \text{ pH}_{\frac{1}{2}} \\ 1/3 \log \frac{V_{aq}}{V_o} - 1/3 \log K^* &= \text{pH}_{\frac{1}{2}} \end{aligned} \quad (4-11)$$

In the situation where the volume of both phases are equal:

$$\text{pH}_{\frac{1}{2}} = -1/3 \log K^*$$

The plots of percent extraction vs pH are shown in Figure 3. By examining the $\text{pH}_{\frac{1}{2}}$ values and the proximity of the Sm, Eu, Gd and Tb curves, it is obvious that it is not possible to separate these elements from each other on a batch basis. This is further borne out by examining the $P_c \beta_3$ values for each element. If we define a separation factor, B, at a particular pH, as

$$B = \frac{D_1}{D_2} \quad (4-12)$$

then using equation 4-1 and recalling that at a particular pH the $[R^-]$ is constant

$$B = \frac{(P_c \beta_3)_1}{(P_c \beta_3)_2} \quad (4-13)$$

If we accept 99% extraction of metal 1 with a corresponding maximum of 1% extraction of metal 2, then

$$B = \frac{D_1}{D_2} = \frac{\frac{99}{1}}{\frac{1}{99}} = \frac{10^2}{10^{-2}} = 10^4 \quad (4-14)$$

and $P_c \beta_3$ for metal 1 must be at least 10^4 times greater than that of metal 2 for separation with a one-stage extraction. The separation factors, calculated from the $P_c \beta_3$ values (Table 8, page 70) are listed in Table 4. It appears that these elements cannot be separated by a one stage extraction.

Using equation 4-2 and at the point where $D = 1$ (50% extraction with equal volumes), then

$$[H^+]^n = P_c \beta_3 K_a^n [HR]^n \quad (4-15)$$

Since $[HR]$ is a constant, it can be seen that $P_c \beta_3$ is related to $\text{pH}_{\frac{1}{2}}$. Thus the difference in $\text{pH}_{\frac{1}{2}}$ values of two metal ions in a

FIGURE 3
Percent Extraction Curves for
Metals Studied

specific system is a measure of the separability of these two ions.

TABLE 4

Table of Separation Factors - B
as Determined by Log P_{cA_3} Values

<u>Combination</u>	<u>Log B</u>	<u>B</u>
Pr - Sm	1.25	18
Sm - Eu	0.17	1.5
Gd - Tb; and Eu - Tb	0.78	6.0
Pr - Tb	2.20	160
Sm - Tb	0.95	9
Gd - Eu	0.0	1

Porell² of this laboratory has determined the extraction curves for scandium, yttrium and lanthanum. The $pH_{\frac{1}{2}}$ for scandium is 1.82 and that of lanthanum is 6.8, while that of yttrium and the lanthanides studied in this work have $pH_{\frac{1}{2}}$ values of 5.2 - 6.2. Thus scandium may be separated from the lanthanides by adjusting pH to about 2 - 3 and the scandium will extract leaving the lanthanides behind in solution.

Separations can sometimes be accomplished by using successive extraction stages or counter current extraction. An examination of Figure 3 shows that there is a theoretical possibility of the separation of terbium and praseodymium by a few successive stages. The separation factor, B, at pH 5.6 is 160. The separation factor

²Porell, A.L., Private Communication.

for terbium and samarium at pH 5.5 is only 9 and thus many more theoretical stages would be required.

III Determination of Formation Constants of Aqueous Species

As pointed out in Chapter III, preliminary work showed very poor extraction when dipivaloyl methane in benzene was used as the organic phase unless the concentration of the reagent was on the order of 1.5 M or greater. This can be explained in terms of equation 4-2. Since the reagent has to distribute itself between the aqueous layer and the benzene layer, the concentration in the aqueous layer is generally well below the saturated level and the distribution ratio will be low. The use of pure reagent as the chelating solvent then should permit extractions at higher aqueous reagent concentrations and thereby at lower pH values. In addition it may affect the partition coefficient of the extracted species. However, it will be recalled that equation 4-2 is valid only in the region where the free hydrated metal ion is the only aqueous species. Equation 3-12, reproduced here as equation 4-16, shows that as other species exist in the aqueous phase, the distribution ratio will tend to decrease.

$$D = \frac{P_c \beta_3 [R]^3}{1 + \sum_j \sum_p \beta_{jp} [R]^j [OH]^p} \quad (4-16)$$

Expanding the denominator for two terms using, for illustrative purposes, the assumption that the two terms have $j = 1$, $p = 0$ and $j = 1$, $p = 1$ and substituting for R in terms of the dissociation constant and aqueous HR concentration gives

$$D = \frac{P_c \mathcal{E}_3^3 K_a^3 [HR]_{aq}^3}{[H^+]^3 + \mathcal{E}_{10} K_a [HR]_{aq} [H^+]^2 + \mathcal{E}_{11} K_a [HR]_{aq} K_w [H^+]} \quad (4-17)$$

Thus at constant reagent concentration, a plot of log D vs pH should give regions of slope 3, 2, 1, etc. where the appropriate aqueous species predominate providing there is sufficient difference between successive formation constants. Thus in a region where an integer slope is obtained over a wide range, only one species can be said to exist.

Nature of Extracted Species

The equations developed are based upon the assumption of a neutral species existing in the organic phase. As pointed out by Morrison and Freiser,³ it is convenient to classify extraction systems on the basis of the nature of the extractable species. In chelate extraction systems, reagent anions easily replace coordinated water from many metals to form neutral essentially covalent chelate compounds. In ion association extraction systems, the extractable species are formed by the association of ions, e.g. $MR_4^-(C_2H_5)_4N^+$ or $MR_2^+ ClO_4^-$. In this study on the lanthanides, an examination of this possibility was made by concentrating the organic species by distillation of the excess reagent and then analyzing for the presence of nitrogen from the $(C_2H_5)_4N^+$ and for the presence of perchlorate. The sodium fusion test as described by Cheronis and

³Morrison, G.H. and Freiser, H., "Solvent Extraction in Analytical Chemistry" (New York: John Wiley and Sons, Inc., 1957), p. 5.

Entrikin⁴ was used to test for nitrogen while the perchlorate test was performed according to the procedure described in Scott's text on analysis.⁵

These tests were performed on the solid material remaining after the DPM was distilled from a collection of many organic phases from the extraction of 2.5×10^{-3} M Eu³. Negative results were obtained in both situations.

In addition, if these species are extracted, there would be an initial slope, at lower pH values, of 2 or 4. This can be seen by equation 4-18, assuming the extracted species is MR_2ClO_4 since all terms in the numerator are constant.

$$D = \frac{P_c \beta_n [R]^2 [ClO_4^-]}{1} = \frac{P_c \beta_n [ClO_4^-] K_a^2 [HR]^2}{[H^+]^2} \quad (4-18)$$

Thus, the extracted species is not an ion association complex and since the extraction shows a dependence upon pH and thus upon reagent anion concentration, the extracted species can be assumed to be a neutral chelate. The only combinations of M, R and CH that are neutral are: $MR(OH)_2$, MR_2CH and MR_3 . As shown in Chapter III and by Brown,⁶ Pope⁷ and others, the presence of a

⁴Cheronis, N.D. and Entrikin, J.B., "Semimicro Qualitative Organic Analysis" (New York: Thomas Y. Crowell Co., 1947), p. 91.

⁵Scott's "Standard Method of Chemical Analysis", ed. N.H. Furman (5th ed.; New York: D. Van Nostrand Co. Inc., 1939), p. 262.

⁶Brown, W.B., et al., J. Inorg. Nucl. Chem., 25 429 (1963).

⁷Pope, G.W., Steinbach, J.F. and Wagner, W.F., J. Inorg. Nucl. Chem., 20 304 (1961).

very large excess of reagent together with the lower solubility of the hydrolyzed species compared to that of the unhydrolyzed species leads, as predicted by Stary,⁸ to the assumption that the only extracted species is MR_3 . Wagner⁹ showed that addition of acetylacetone to solid monobasic lanthanide chelate $[LnCH(C_5H_7O_2)_2]$ converted it to the monohydrated compound $Ln(C_5H_7O_2)_3 \cdot H_2O$.

Attempts to concentrate and recover the extracted species by techniques such as distillation, sublimation, crystallization, etc., were not considered to be definitive due to the possibility of obtaining a species that was not the actual extracted species existing in the organic phase at equilibrium. The concentration of the metal used (10^{-5} M) was too low to definitely show the presence of an CH in the organic phase (~ 4.9 M) although NMR and IR determinations were done and no OH was found. These determinations were done on the organic phase as extracted and also on the concentrated organic phase after distilling off most of the excess reagent from 10^{-3} M solutions.

Extracted samples of 0.08 M europium in pure DPM were injected into a gas chromatographic column under the following conditions: 15 cm column of 10% Apiezon N on Gas Pak F, column temperature 168° C., flame ionization detector, injection port 230° C., detector temperature 280° C., He flow 100 ml/min. This is the same column used by Eisentraut and Sievers¹⁰ in their

⁸Stary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p. 12.

⁹Wagner, W.F., Record of Chem. Prog., 23 155 (1962).

¹⁰Eisentraut, K. and Sievers, R.E., J. Am. Chem. Soc., 87 5254 (1965).

separation of the tris lanthanide chelates of dipivaloyl methane. A single peak was found at 17 minutes retention time, in addition to the dipivaloyl methane peak immediately after injection. The europium tris chelate, $\text{Eu}(\text{DPM})_3$, prepared by Kauffman of this laboratory according to the procedure of Eisentraut and Sievers,¹¹ was dissolved in acetone and injected into the column with the same resulting retention time.

An attempt was made to perform calculations assuming the presence of both MR_3 and MR_2OH in the organic phase. If both species exist, then an equation can be written for the region where M^3 is essentially the only species in the aqueous phase.

$$D = \frac{P_c \beta_{30} [\text{R}]^3 + P_{c_1} \beta_{21} [\text{R}]^2 [\text{OH}]}{1} \quad (4-19)$$

This equation is directly analogous to equation 4-1 and the same assumptions are involved.

The use of simultaneous equations or determinants in the pH range 5 - 6 did not permit the determination of both $P_c \beta_{30}$ and $P_{c_1} \beta_{21}$ and indicates that the existence of both species in the organic phase cannot be mathematically justified with the data obtained.

It seems that, within the detectability limits of the methods used, the assumption that MR_3 is the only extracted species in the organic phase can be made.

Some extracted species may contain one or two molecules of the reagent as molecules of solvation. In extraction systems where

¹¹Ibid.

the reagent is dissolved in another organic solvent such as benzene, chloroform, etc., it is possible to vary the reagent concentration and thus to determine the dependence of $\log D$ on the reagent concentration. As shown by Schweitzer and VanWillis,¹² a plot of $\log D$ vs $\log [HR]_{org}$ generally gives a straight line of constant slope at a constant pH. If the slope equals the charge on the free hydrated ion, then the extracted species is MR_n . If the slope is greater than the charge, then the difference indicates the number of molecules of reagent HR included in the extracted species, e.g., $MR_A(HR)_A$.

However, when the reagent is used as a chelating solvent, the ability to vary the reagent concentration is removed and some definition in the system is lost. As pointed out by Schweitzer and VanWillis,¹³ if a species such as $MR_R(HR)_A$ is dominant in the organic phase, then, since HR is also the solvent and A is not uniquely determined, the HR dependence can be included in the $P_c \phi_3$ product.

Consideration of Possible Species

In order to determine formation constants of the species existing in the aqueous phase, it is necessary to use equation 4-16 in connection with the $\log D$ vs pH curves shown in Figures 4 to 8. $\log D$ vs pR ($-\log [R]$) curves are shown in Figures 9 to 12

¹²Schweitzer, G.K. and VanWillis, W., "Advances in Analytical Chemistry and Instrumentation" (New York: John Wiley and Sons, Inc., 1966), Vol. V, p. 169.

¹³Schweitzer, G.K. and VanWillis, W., Anal. Chim. Acta, 36 77-89 (1966).

FIGURE 4

Log D vs pH Curve
for Praseodymium

Experimental points ϕ

Calculated curve ———

Best line through data - no calculation - - - - -

FIGURE 5

Log D vs pH Curve
for Samarium

Experimental points
Calculated curve

FIGURE 6

Log D vs pH Curve
for Europium

Experimental points
Calculated curve

FIGURE 7

Log D vs pH Curve
for Gadolinium

Experimental points

Calculated curve

FIGURE 8

Log D vs pH Curve
for Terbium

Experimental points

Calculated curve

FIGURE 9

Log D vs pR Curve
for Samarium

Experimental points
Calculated curve

FIGURE 10

Log D vs pR Curve
for Europium

Experimental points
Calculated curve

FIGURE 11

Log D vs pR Curve
for Gadolinium

Experimental points
Calculated curve

FIGURE 12

Log D vs pR Curve
for Terbium

Experimental points
Calculated curve

for comparison. Equation 4-16 can perhaps be simplified by an examination of literature values concerning the first acid ionization constant of the hydrated metal cation. Moeller¹⁴ gives values for K_a in the range of 2.5×10^{-9} to 0.5×10^{-9} for Gd^{+3} to Pr^{+3} . This gives β_{01} (formation constant for the reaction $M(H_2O)_n^{+3} + OH^- \rightleftharpoons M(H_2O)_{n-1}OH^{+2} + H_2O$) on the order of 2.5×10^5 to 5×10^4 . Larsen¹⁵ in his book on transitional elements reports constants of $1 - 1.3 \times 10^{-9}$ for the elements Ce^{+3} to Gd^{+3} . This gives $\beta_{01} = 1 - 1.3 \times 10^5$. Tobias and Garrett¹⁶ report a K_a value of about 3×10^{-9} for the following reaction of Nd^{+3} and Pr^{+3} .

Rewriting equation 4-16 in terms of only the first hydrolysis species

$$D = \frac{P_c \beta_3 [R]^3}{1 + \beta_{01} [OH^-]}$$

it is obvious that an $[OH^-]$ of at least 4×10^{-7} is necessary to have a value large enough to be significant. This is equivalent to a pH of 7.6. As can be seen by examining Figures 4 to 8, the slope of the log D vs pH plot has changed from 3 before this pH is reached. Therefore, it can be concluded that some other species

¹⁴Moeller, T., J. Phys. Chem., 50 242 (1946).

¹⁵Larsen, E.M., "Transitional Elements" (New York: W.A. Benjamin, Inc., 1965), p. 103.

¹⁶Tobias, R.S. and Garrett, A.B., J. Am. Chem. Soc., 80 3532 (1958).

is formed in the aqueous phase before the concentration of MOH^{+2} becomes significant. Thus in analyzing the curve, the existence of MOH^{+2} can be neglected.

Further examination of Figures 4 to 8 shows only one region where the slope is an integer over a wide range of pH values. This region is at high pH and shows a slope of -2. This indicates the existence of a doubly negative species predominating in the aqueous phase. Furthermore, it can be seen that there is no region where definite slopes of +2 and +1 exist, indicating that the formation constants for the first two aqueous species are close together.

Several methods for the analysis of these curves have been proposed and discussed by Rossotti and Rossotti,¹⁷ Stary,¹⁸ Dyrssen and Sillen¹⁹ and Rydberg.²⁰ However, each of these methods is only as good as the assumed equation.

As shown by Rydberg,²¹ Schweitzer and VanWillis²² and others, much information can be gathered concerning the system if one determines D as a function of pH and pR concentration. For example, Rydberg shows that D will be a function of pR in the region where

¹⁷Rossotti, F.J.C. and Rossotti, H., "Determination of Stability Constants" (New York: McGraw Hill, 1961), Chap. 5 & 10.

¹⁸Stary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p.15.

¹⁹Dyrssen, D. and Sillen, L.G., Acta Chem. Scand., 7 663 (1953).

²⁰Rydberg, J., Acta Chem. Scand., 14(1) 157 (1960).

²¹Ibid.

²²Schweitzer, G.K. and VanWillis, W., "Advances in Analytical Chemistry and Instrumentation" (New York: John Wiley and Sons, Inc., 1966), Vol. V., p. 180.

complexes of the type MR_n are formed and a function of pR and HR concentration in the region where $MR_n(OH)_p$ type complexes are formed. However, the ability to vary the HR concentration is lost when HR is used as a chelating solvent. It is therefore necessary to use chemical and logical considerations in developing the equations needed to solve for the necessary formation constants.

An examination of the $[OH^-]$ and $[R^-]$ at various pH values as determined from the solubility and dissociation constant for dipivaloyl methane was made and the results are shown in Table 5. It is quite evident therefore that there is no pH region where either ion predominates strongly over the other and thus the possibility of hydroxy chelate complexes $MR_j(OH)_p$ must be considered throughout all areas of the distribution curve.

In view of the above, it is concluded that the aqueous species must start with the free hydrated metal ion and then form a MR complex as the next stepwise species. Other species cannot be as readily determined. A listing of possible species that may be present is shown in Table 6.

The MR_5 species was eliminated on the basis that it is sterically unlikely to exist. While the tetrakis chelate of lanthanides and DPM have not been reported, those of dibenzoylmethane and similar beta diketones have been prepared.^{23,24} In addition,

²³Bauer, H., Blanc, J. and Ross, D.L., J. Am. Chem. Soc., 86 5125 (1964).

²⁴Melby, L.R., Rose, N.J., Abramson, E. and Caris, J.C., J. Am. Chem. Soc., 86 5117 (1964).

TABLE 5

Concentration of DPM^- and CH^- as a Function of pH

pH	$[\text{OH}^-]$	$[\text{DPM}^-]$	$[\text{OH}^-]/[\text{DPM}^-]$
3.0	1×10^{-11}	1.61×10^{-12}	6.2
4.0	1×10^{-10}	1.61×10^{-11}	6.2
5.0	1×10^{-9}	1.61×10^{-10}	6.2
6.0	1×10^{-8}	1.61×10^{-9}	6.2
7.0	1×10^{-7}	1.61×10^{-8}	6.2
8.0	1×10^{-6}	1.61×10^{-7}	6.2
9.0	1×10^{-5}	1.68×10^{-6}	5.95
9.5	3.16×10^{-5}	6.05×10^{-6}	5.22
10.0	1×10^{-4}	2.33×10^{-5}	4.3
10.5	3.16×10^{-4}	1.12×10^{-4}	3.8
11.0	1×10^{-3}	6.01×10^{-4}	1.66
11.5	3.16×10^{-3}	2.69×10^{-3}	1.17
12.0	1×10^{-2}	9.22×10^{-3}	1.08
12.5	3.16×10^{-2}	2.35×10^{-2}	1.34

TABLE 6

Species that May Be Present in Aqueous Phase

Charge on Species					
3	2	1	0	-1	-2
M	MR	MR_2	MR_3	MR_4	MR_5
		MROH	MR_2OH	MR_3OH	MR_4OH
			$\text{MR}(\text{OH})_2$	$\text{MR}_2(\text{OH})_2$	$\text{MR}_3(\text{OH})_2$
				$\text{MR}(\text{OH})_3$	$\text{MR}_2(\text{OH})_3$
					$\text{MR}(\text{OH})_4$

the $\text{Zr}(\text{DPM})_4$ has been prepared, with some difficulty, by repeated treatments of zirconium acetylacetonate with dipivaloyl methane.²⁵ Thus, under the conditions of this experiment, and considering the steric hindrance of the t-butyl groups, it is considered unlikely that an MR_5 complex would be formed.

All other species of charge -2 must be considered possible since they represent coordination numbers of 6 - 9, all of which have been reported for the lanthanides.²⁶

A series of distribution equations can be written, of the form shown in equation 4-16, in which one species for each charge is used (shown in Table 6) and adjacent species differ by only one R or one OH. These equations would then show possible combinations of species that predominate in the aqueous phase and the equation can then be solved for the individual formation constants. There are fifteen combinations possible which are listed in Table 7, showing only the aqueous species.

Determination of $P_c \beta_3$ Values

It is possible to determine the product, $P_c \beta_3$, as an entity rather than considering it as two separate unknowns or having to make any estimates concerning the value of the partition coefficient,

²⁵ Sievers, R.E., Eisentraut, K.J., Meek, D.W. and Springer, Jr., C.S., *Advances in Chemistry*, In Press, 1967.

²⁶ Moeller, T., et al., *Chem. Reviews*, 65(1) 1 (1965).

TABLE 7
Combinations of Aqueous Species

M	MR	MR ₂	MR ₃	MR ₄	MR ₄ OH
M	MR	MR ₂	MR ₃	MR ₃ OH	MR ₄ OH
M	MR	MR ₂	MR ₃	MR ₃ OH	MR ₃ (OH) ₂
M	MR	MR ₂	MR ₂ OH	MR ₃ OH	MR ₄ OH
M	MR	MR ₂	MR ₂ OH	MR ₃ OH	MR ₃ (OH) ₂
M	MR	MR ₂	MR ₂ OH	MR ₂ (OH) ₂	MR ₃ (OH) ₂
M	MR	MR ₂	MR ₂ OH	MR ₂ (OH) ₂	MR ₂ (OH) ₃
M	MR	MROH	MR ₂ OH	MR ₃ OH	MR ₄ OH
M	MR	MROH	MR ₂ OH	MR ₃ OH	MR ₃ (OH) ₂
M	MR	MROH	MR ₂ OH	MR ₂ (OH) ₂	MR ₃ (OH) ₂
M	MR	MROH	MR ₂ OH	MR ₂ (OH) ₂	MR ₂ (OH) ₃
M	MR	MROH	MR(OH) ₂	MR ₂ (OH) ₂	MR ₃ (OH) ₂
M	MR	MROH	MR(OH) ₂	MR ₂ (OH) ₂	MR ₂ (OH) ₃
M	MR	MROH	MR(OH) ₂	MR(OH) ₃	MR ₂ (OH) ₃
M	MR	MROH	MR(OH) ₂	MR(OH) ₃	MR(OH) ₄

P_c. In fact, several authors have used this product as a measure of the extraction efficiency of various systems.^{27,28,29}

This value can be easily determined using equation 4-1 which is valid in the pH region where only free hydrated metal ion

²⁷Wagner, W.F., Record of Chem. Prog., 23 155 (1962).

²⁸Stary, J. and Hladky, E., Anal. Chim. Acta, 28 227 (1963).

²⁹Schweitzer, G.K. and VanWillis, W., Anal. Chim. Acta, 36 77-89 (1966).

exists in the aqueous phase. The $\log P_c \beta_3$ values determined in this way are listed in Table 8, where $\log P_c \beta_3$ are those values obtained as the average of values determined at several points in the low pH region and $\log P_c \beta_3$ (calc.) are those calculated at the $\text{pH}_{\frac{1}{2}}$ point from equation 4-20. This equation was derived from equation 4-2 by using the $\text{pH}_{\frac{1}{2}}$ values where $D = 1$ if $V_{\text{aq}} = V_{\text{org}}$ or 2 if $V_{\text{aq}} = 2 V_{\text{org}}$.

$$\log P_c \beta_3 = \log 2 - 3 \text{pH}_{\frac{1}{2}} + 3 \text{pK}_a - 3 \log [\text{HR}]_{\text{aq}}$$

where $V_a = 2 V_o$ (4-20)

TABLE 8
 $P_c \beta_3$ Values

Lanthanide	$\log P_c \beta_3$	$\log P_c \beta_3$ (calc.)
Pr	26.20 ± 0.07	26.07
Sm	27.45 ± 0.07	27.57
Eu	27.62 ± 0.07	27.75
Gd	27.62 ± 0.07	27.70
Tb	28.40 ± 0.07	28.47

Schweitzer and VanWillis³⁰ suggest that the best basis for direct comparison between chelating solvents is the value of this product $P_c \beta_3$ (called two phase stability constant by Stary³¹) for each metal with each chelating solvent.

A high value of $\log P_c \beta_3$ should indicate a better extraction

³⁰Schweitzer, G.K. and VanWillis, W., Anal. Chim. Acta, 36 77-89 (1966).

³¹Stary, J., Anal. Chim. Acta, 28 132 (1963).

system when comparing chelating solvents. Little information has been published concerning $P_c \beta_3$ values for the lanthanides in chelating solvents. Schweitzer and VanWillis³² list some $\log P_c \beta_3$ values for promethium (III) with 2,4 pentanedione (22.5), 7-methyl-2,4-octanedione (MOD) (23.8) and 1,1,1-trifluoro-7-methyl-2,4-octanedione (FMOD) (29.7). The aqueous concentrations of the last two reagents are about three to four times higher than that of 2,2,6,6-tetramethyl 3,5-heptanedione (DPM) determined in this work but the pK_a values are 9.72 for MOD and 7.14 for FMOD. Thus, these are apparently slightly better chelating solvents for lanthanides than is dipivaloyl methane.

Determination and Discussion of Extraction Constant

Another method of comparing extraction systems is the use of the overall extraction constant K defined by Dyrssen,³³ Stary³⁴ and others, based on the overall stoichiometric relationship

$$K = \frac{[MR_{N_{org}}]_o [H^+]^N}{[M^{+N}] [HR]_o^N} \quad (4-22)$$

Making use of the $P_c \beta_3$ and P , the partition coefficient of the reagent, which relationships were defined earlier, this equation can be converted to

³²Schweitzer, G.K. and VanWillis, W., Anal. Chim. Acta, 36 77-89 (1966).

³³Dyrssen, D., Svensk. Kemisk. Tidskrift, 68 212 (1956).

³⁴Stary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p. 21.

$$K = \frac{D [H^+]^3}{[HR]_o^3} = \frac{P_c \mathcal{E}_3 [R]^3 [H^+]^3}{[HR]_o^3} = \frac{P_c \mathcal{E}_3 K_a^3}{P^3} \quad (4-23)$$

with the understanding that it applies in the region where only free hydrated metal ion exists in the aqueous phase, and assuming equal phase volumes. A knowledge of the extraction constant, K , for a system enables one to calculate the D value for every value of $[HR]_{org}$ and pH . However, the value of K is dependent upon the distribution coefficient P_c and the concentration of the reagent in the organic phase. Most extraction systems involve the use of the reagent dissolved in an organic phase such as benzene or chloroform and the extraction constant is of value when comparing different reagent concentrations in the same solvent or the same reagent concentration in different solvents, etc., providing, in the latter case, the value of P does not change much. Thus, in all systems, it is possible to compare these K values but the individual variables for the two systems are needed in order to ascertain the controlling factors. Log K 's for the elements extracted in this study are listed in Table 9.

TABLE 9
Overall Extraction Constant K

<u>Element</u>	<u>Log K</u>
Pr	-20.36
Sm	-18.9
Eu	-18.7
Gd	-18.7
Tb	-18.0

Comparison of these values with some of the few reported for other systems of the lanthanides as listed in Table 10 indicates that DPM as a chelating solvent is of about the same efficiency as others listed except for TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) which is known as a much more effective chelating agent.

TABLE 10

Extraction Constants of Some Lanthanides with Some -diketones

System	Log K	Reference
Pr(III) 0.2 M TTA-C ₆ H ₆	-8.48	1
La(III) 0.2 M TTA-C ₆ H ₆	-10.5	2
Eu(III) 0.1 M TTA-C ₆ H ₆	-7.66	4
Gd(III) 0.1 M TTA-C ₆ H ₆	-7.57	4
Tb(III) 0.1 M TTA-C ₆ H ₆	-7.51	4
La(III) 0.1 M Benzoylacetone-C ₆ H ₆	-20.5	2,3
La(III) 0.1 M Dibenzoylmethane-C ₆ H ₆	-19.5	2,3
Eu(III) 0.1 M Benzoylacetone-C ₆ H ₆	-18.9	5
La(III) 0.1 M Benzoylacetone-CHCl ₃	-21.81	5

¹Keenan, T.K. and Suttle, J.F., J. Am. Chem. Soc., 76 2184 (1954).

²Ruzicka, J. and Sary, J., Talanta, 10 287-293 (1963).

³Sary, J. and Hladky, E., Anal. Chim. Acta, 28 227 (1963).

⁴Poskanzer, A.M. and Foreman, Jr., B.M., J. Inorg. Nucl. Chem., 16 323 (1961).

⁵Sary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p. 61.

In solving the distribution equation for overall formation constants, β_n , it is necessary to know the value of the chelate distribution coefficient, P_c . If the plot of $\log D$ vs pH (or pR) shows an extensive range of slope = 0, it is assumed that the predominant aqueous phase species is MR_3 . The equation then is:

$$D = \frac{P_c \beta_3 [R]^3}{\beta_3 [R]^3} \quad (4-24)$$

and the assumption is made that $D = P_c$. In this study, a range where slope = 0 was not found but the quantity $P_c \beta_3$ as determined above can be treated as a single unknown until β_3 is determined.

On the $\log D$ vs pH plots shown, a range is found where there is a slope of -2 and thus a species of charge -2 predominates in the aqueous phase. Examining the possible species listed in Table 6 and recalling that the R and OH concentrations (Table 5) are practically equal in this pH range, it is apparent that there is no way to determine if any species can be eliminated from consideration. The distribution equation can be written to show only the -2 charged species in the aqueous phase as follows:

$$\begin{aligned} D &= \frac{P_c \beta_3 [R]^3}{\beta_{14} [R] [CH]^4} & D &= \frac{P_c \beta_3 [R]^3}{\beta_{23} [R]^2 [OH]^3} \\ D &= \frac{P_c \beta_3 [R]^3}{\beta_{32} [R]^3 [OH]^2} & D &= \frac{P_c \beta_3 [R]^3}{\beta_{41} [R]^4 [OH]} \end{aligned} \quad (4-25)$$

It is possible therefore to get first approximations for β_{14} , or β_{23} , or β_{32} or β_{41} from equation 4-25 assuming each species is the only one present.

Values of $P_c \beta_3$ and β_{14} or β_{23} or β_{32} or β_{41} have now been determined. Several attempts were made to solve for β_{10} and β_{20} or β_{10} and β_{11} values in the pH range of approximately 6 - 8. This is the range where MR and MR₂ or MR and MRCH should exist as evidenced by the slope of the curve log D vs pH. If the species MR₂ or MRCH predominated in the aqueous phase, the slope should be 1. An examination of the log D vs pH curves shows slopes of 3, 2 and 1 very close together. Thus, it is apparent that there is no pH region where MR species predominates or exists to any great extent.

The following methods were used in an attempt to solve for these constants: simultaneous equations, limiting value method of Leden and determination of the least sum of the squares of the deviations as β_{10} and β_{20} or β_{10} and β_{11} were varied. This last technique involves the determination of the difference between the observed D value and the calculated D value when values of β_{10} and β_{20} (or β_{10} and β_{11}) are varied. These differences are squared and summed over all the data points. These differences are plotted for each combination of β_{10} and β_{20} used and contour lines drawn through points of equal sum square values. In this way, a "pit map" can be drawn and by repeated calculations the best and most refined value for the combination of β_{10} and β_{20} can be determined as being that combination that gives the least sum square of the deviation.

All attempts indicated that a reliable value for β_{10} could not be determined. The use of simultaneous equations and the limiting value method led to negative β_{10} values. The least sum

of the squares of the deviations led to values where the least sum square was found to be essentially the same over a very small range of β_{20} or β_{11} values as β_{10} was varied over a wide range. This information was interpreted as due to the probability that the formation constants k_1 and k_2 for the stepwise formation of these two species were fairly close together so that the second intermediate chelate was formed very quickly after the first one and the data obtained by solvent extraction procedures do not permit the separation of these two constants. This is the conclusion arrived at by Sullivan, Rydberg and Miller³⁵ and Rydberg³⁶ using weighted least squares calculations to determine complexity constants. They found that it was possible to obtain proper fits of data using fewer stepwise species than postulated. For example, if calculations led to a negative value or to a value whose standard deviation was greater than the measured value, this species was dropped from consideration and the values were recalculated.

It must be stressed that this procedure of eliminating certain complexes from consideration does not necessarily mean that these complexes do not exist, but only that the equilibrium constants cannot be calculated because of uncertainties in the experimental data or because the species does not exist to a great extent.

Approximate values of β_{10} were determined by assuming $k_1 = k_2$ and determining the fit with the log D vs pH curves. A fairly wide range of β_{10} values were found to fit the curve due

³⁵Sullivan, J.C., Rydberg, J. and Miller, W.F., Acta Chim. Scand., 13(10) 2023 (1959).

³⁶Rydberg, J., Acta Chim. Scand., 14(1) 157 (1960).

to the fact that the species never predominates for a long time and thus does not affect the log D vs pH data significantly. This is why a large deviation is found as shown in Table 11.

The use of only β_{20} or β_{11} adequately describes the extraction curve in the lower pH region until the next stepwise complex becomes effective, and it is not possible in this system to distinguish between β_{20} or β_{11} .

Formation constants for the remainder of the possible combinations listed in Table 7 were evaluated initially using iterative computer techniques. It was found that the combinations used above could not adequately describe the experimental data. In the area between MR_2 (or $MRCH$) and the negatively 2 charged species (i.e., where $MR(OH)_2$, MR_2OH or MR_3 and a negative 1 species predominate) calculated curves could not be made to agree with the experimental curve throughout the entire region, assuming only one neutral species present. The assumption that MR_2OH or MR_3 are the only neutral species existing in the aqueous phase led to β_{30} values that gave the best fit of calculated D values that agreed with the top of the curves ($\sim$ pH 10 - 11) but were too high in the pH 8.5 - 10 range approximately. Assuming only MR_2OH , the best fit (least sum of squares of deviation) gave β_{21} values that yielded calculated D values that were slightly high at pH 10 - 11 range and too low in the 8.5 - 10 pH range. When $MR(OH)_2$ was assumed to be the only neutral aqueous species, a close fit could not be obtained at all. The best calculated D values were much too high in the pH 10 - 11 range or much too low in the 8.5 - 10 pH range. Corrections to all these species could not be made by

increasing β values of the -1 charged species as this caused too low D values in the pH 11 - 12 range.

The above calculations led to two conclusions:

1. The data could not be adequately explained by assuming the presence of only one neutral species in the aqueous phase.
2. The negative one charged species must exist only briefly. The calculations therefore confirm the slope of the log D vs pH curve in the pH 11 region where there is an abrupt change of slope from zero to almost -2 over a range of about 0.5 pH unit.

Calculations were repeated assuming both MR_2OH and MR_3 or $MR(OH)_2$ and MR_2OH as the most likely combinations of neutral species in the aqueous phase. The least sum of squares of the deviations iterative technique was used again. This led to excellent agreement throughout the entire curve for the systems assuming that both MR_2OH and MR_3 are present in the aqueous phase. This agreement is shown in Figures 4 to 8 where the solid line is the curve calculated using the beta values shown in Table 11. The other combination of $MR(OH)_2$ and MR_2OH did not give agreement. The least sum square of the deviation technique led to values where the least sum square was found to be essentially the same over a very small range of β_{21} values as β_{12} was varied over a wide range. In addition, it was noted that the best fits were obtained when β_{21} was of the order of 10^{22} and β_{12} was of the order of 10^{18} . The best calculated D values obtained were a little high in the 10.5 - 11 pH range and low in the 8.5 - 10.5 pH range and the D

TABLE 11
Log of Overall Formation Constants
Temperature - 24 $^{\circ}$ C.

Constant	Element				
	Pr	Sm	Eu	Gd	Tb
$P_c \beta_3$	26.50 $\pm$.07	27.47 $\pm$.07	27.62 $\pm$.07	27.62 $\pm$.07	28.40 $\pm$.07
β_{10}^{**}	8.20 $\pm$.15	8.30 $\pm$.15	8.35 $\pm$.15	8.30 $\pm$.15	8.46 $\pm$.15
β_{11}	15.52 $\pm$.05	15.73 $\pm$.05	15.86 $\pm$.05	15.73 $\pm$.05	16.07 $\pm$.05
β_{20}	16.3 $\pm$.05	16.50 $\pm$.05	16.60 $\pm$.05	16.53 $\pm$.05	16.86 $\pm$.05
β_{21}	*	22.05 $\pm$.06	22.08 $\pm$.06	22.10 $\pm$.06	22.57 $\pm$.06
β_{30}	*	22.28 $\pm$.06	22.34 $\pm$.06	22.37 $\pm$.06	22.93 $\pm$.06
β_{31}^{**}	*	24.7 $\pm$.25	24.7 $\pm$.25	24.7 $\pm$.25	25.0 $\pm$.25
β_{22}^{**}	*	24.7 $\pm$.25	24.7 $\pm$.25	24.7 $\pm$.25	25.0 $\pm$.25
β_{40}^{**}	*	24.7 $\pm$.25	24.7 $\pm$.25	24.7 $\pm$.25	25.0 $\pm$.25
β_{41}	*	27.83 $\pm$.09	27.94 $\pm$.09	28.16 $\pm$.09	28.55 $\pm$.10
β_{32}	*	27.79 $\pm$.09	27.90 $\pm$.09	28.12 $\pm$.09	28.47 $\pm$.10
β_{23}	*	27.76 $\pm$.09	27.87 $\pm$.09	28.09 $\pm$.09	28.43 $\pm$.10
P_c	*	5.17	5.28	5.25	5.47

Note: With the exception of the $P_c \beta_3$, β_{21} , β_{30} and P_c values, all values were calculated on the assumption that that species was the only one of that charge present. See text for further explanation.

* Due to the low radiometric counting rate and short half life of the isotope used in this study (^{143}Pr), the counting errors were extremely large and no meaningful values for these constants could be calculated.

** The large estimated error involved in these constants is a direct consequence of their brief existence. See text for further explanation.

values did not show much dependence upon variation of assumed β_{12} values. In view of this lack of fit, it can be concluded that the experimental data can only be explained by the presence of both neutral species, MR_2OH and MR_3 , in the aqueous phase and eliminates any sequence of stepwise formations involving the presence of $MR(OH)_2$ as a significant specie. This therefore eliminates the likelihood of an $MR(OH)_3$ and $MR(OH)_4$. The presence of MR_2OH and MR_3 lends weight to the probability that MR_2 is the 1 charged species but does not eliminate the possibility that $MROH$ may also be present.

It is not possible, mathematically, to distinguish between the possible -1 and -2 charged species and thus to eliminate any. Attempts to assume the presence of two species simultaneously in the region where the slope is -2 were unsuccessful. Considering the presence of both MR_2OH and MR_3 in the aqueous phase, the addition of either one R or one OH to each species leads to the following possibilities:

Considering the steric effects involved in placing a fourth dipivaloyl methane with its bulky t-butyl groups on a trivalent lanthanide and considering the fact that Bauer, Blanc and Ross³⁷ were unable to prepare $Eu(DPM)_4^-$ using their technique involving the reaction of a mixture of 4:1 ligand to metal and considering

³⁷Bauer, H., Blanc, J. and Ross, D.L., J. Am. Chem. Soc., 86 5125 (1964).

the technique used by Sievers et al.³⁸ to make $\text{Zr}(\text{DPM})_4$, it seems unlikely that an MR_4^- species is formed under the conditions of this study. Also the formation of MR_4^- as the only negative 1 species would appear to be rather difficult from MR_2OH . However, there is no independent evidence to eliminate this species and its obvious successor MR_4OH but it is considered unlikely to be present to any great extent.

The other two possible singly charged negative species listed above are both likely and cannot be distinguished in this system. This same line of reasoning can be applied to the area where the negative 2 species exists. This gives the following possibilities:

Again it is not possible in this system to definitively determine the specie(s) that exist. It would seem likely for several reasons that the most likely species would be either $\text{MR}_3(\text{OH})_2$ or $\text{MR}_2(\text{OH})_3$.

1. In view of the difficulty in making MR_4^- mentioned above, it is not likely that MR_4OH would exist to any great extent.

2. The $\text{MR}_3(\text{OH})_2$ can be formed from either the MR_3CH or the $\text{MR}_2(\text{CH})_2$ species if both can exist in the aqueous phase but MR_3OH can be formed from both MR_3 and MR_2OH .

³⁸Sievers, R.E., Eisentraut, K.J., Meek, D.W. and Springer, Jr., C.S., Advances in Chemistry, 1967, In Press.

Considering the relative concentrations of the OH^- to the DPM^- listed in Table 5 for this pH region (a little greater than 1) both MR_3OH and $\text{MR}_2(\text{OH})_2$ may be present. This also means that $\text{MR}_2(\text{OH})_3$ may be present with the $\text{MR}_3(\text{OH})_2$.

3. The coordination number of the $\text{MR}_2(\text{OH})_3$ specie is 7 while that of $\text{MR}_3(\text{OH})_2$ is 8. Moeller,³⁹ in his review article on Coordination Chemistry of Yttrium and the Rare Earth Metal Ions summarizes evidence for the existence of coordination numbers 7, 8 and 9 and perhaps even 10 among the lanthanide elements. Cunningham, Sands and Wagner⁴⁰ have recently reported the first x-ray crystallographic study of a tris lanthanide (III) chelate and showed that the yttrium ion in $[\text{Y}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (acac = the uninegative ion of 2,4 pentanedione) is eight coordinate. Halverson, Brinen and Leto⁴¹ have indicated the existence of coordination number 8 by preparing $\text{Eu}(\text{DPM})_3(\text{TOPO})_2$ where DPM = dipivaloyl methane and TOPO = trioctyl phosphine oxide.

A representative distribution diagram of the fraction of each species present as a function of pH is shown in Figure 13. This figure is for the europium system and is for the assumption that M, MR_2 , MR_2OH , MR_3 , MR_3OH and $\text{MR}_3(\text{OH})_2$ are the species present. Other combinations give similar diagrams as do the other elements

³⁹Moeller, T. et al., Chem. Review, 65(1) 1 (1965).

⁴⁰Reference 6 of Sievers, R.E., et al., "Volatile Rare Earth Chelates of -diketones", Advances in Chemistry, 1967, In Press.

⁴¹Halverson, F., Brinen, J.S. and Leto, J.R., J. Chem. Phys., 40 2790 (1964).

FIGURE 13

Distribution of Europium Present as Each Species
in the Aqueous Phase
as a Function of pH

studied. This figure shows a slight assymetry in the MR_2 species indicating the existence of an MR specie which could not be separated. The MR_3 curve is a result of the low R^- concentration compared to OH^- and also perhaps because of steric influences hindering the ease of formation of the MR_3 complex. In addition, the increased amount of the MR_3 complex in the pH range 10 - 11 is a result of the increased R^- concentration due to two factors:

1. An increase in solubility of the dipivaloyl methane is occurring in this range.
2. The pH range is now within two pH units of the pK_a value of the reagent which means the reagent is now starting to ionize significantly.

This increased R^- concentration is represented in Table 5 where it can be seen in the decreasing ratio of $[OH^-]$ to $[DPM^-]$ and also in Figure 14 where the ratio of two successive $[DPM^-]$ increments of 0.2 pH units is plotted vs pH. This shows an increase in the rate at which DPM^- is being formed and corresponds to the same pH region where an increased fraction of the MR_3 complex exists.

A diagram of the same species as a function of pR ($-\log R$) shown in Figure 15 indicates a fairly linear increase as a function of $[DPM^-]$. Figure 13 also confirms the validity of the assumption of no significant amounts of hydroxy species or intermediate chelates at the $pH_{\frac{1}{2}}$ value.

A comparison of the formation constants with those obtained by other workers with other ligands can be made only with difficulty due to the lack of complete data for all the lanthanides

FIGURE 14

Rate of Increase of Dipivaloyl Methane Concentration
pH Range 8.5 - 11

FIGURE 15

Distribution of Europium Present as Each Species
in the Aqueous Phase as a Function of pR

with many β -diketones. Moeller's review article⁴² summarized formation constants for many ligands but only three β -diketones. In this article, a complete study was reported for acetylacetone (2,4 pentanedione) but only with La^{+3} , Pr^{+3} and Y^{+3} for benzoylacetone and with La^{+3} , Pr^{+3} , Nd^{+3} and Y^{+3} for propionylacetone. The latter two were in a 75% acetone medium. A few other constants have been reported for isolated β -diketone ligands and elements but no systematic study has been made.

However, as Moeller points out, it is not wise to interpolate or extrapolate in systems where only a few of the rare earth metal ions have been studied. Most correlation plots reported in the literature, such as that shown by Moeller⁴³ or Grenthe and Fernelius⁴⁴ or that of Izatt,⁴⁵ show $\log k_1$ plotted against some function such as electronegativity, ionic radius, etc. This is generally because successive formation constants involve other factors such as stereochemistry, reduced effective charge of the immediate precursor, etc. and k_2 and successive constants cannot be as readily correlated as the first formation constant. Unfortunately, reliable first formation constants could not be obtained in this study. A comparison of the $\log k_2$ and $\log k_1$ values obtained by others is given in Table 12.

⁴²Moeller, T., et al., Chem. Rev., 65(1) 1 (1965).

⁴³Ibid.

⁴⁴Grenthe, I. and Fernelius, W.C. "Formation Constants and Magnetic Behavior of Some Rare Earth Chelates", Rare Earth Research, ed. Eugene V. Kleber, (New York: The MacMillan Co., 1961), p. 12.

⁴⁵Izatt, R.M., Fernelius, W.C., Reed, Jr., C.G. and Block, B.P., J. Phys. Chem., 59 170 (1955).

TABLE 12

Log β_2 and Log β_3 Values for Some β -diketones
and β -diketone-like Ligands

Ligand	Element				Medium	Ref.
	Sm	Eu	Gd	Tb		
Acetylacetone						
β_2	10.4	10.5				1
β_3	13.6	14.0				
Acetylacetone						
β_2	10.05	10.35	10.38	10.63	0.1 M NaClO ₄	2
β_3	12.95	13.64	13.79	14.04		
Dipicolinic						
acid* β_2	15.88	15.98	16.06	16.11	0.5 M NaClO ₄	2
β_3	21.23	21.49	21.83	22.03		
Benzoylacetone						
β_3		14.1				3
Benzoylacetone						
β_2		17.36			3:1 Ethanol Methanol	4
β_3		23.25				

* Reported by authors of reference to be chelated through the carboxyl oxygen.

¹Izatt, R.M., Fernelius, W.C., Haas, Jr., C.G. and Block, B.P., J. Phys. Chem., 59 170 (1955).

²Grenthe, I. and Fernelius, W.C., "Rare Earth Research", ed. Eugene V. Kleber, (New York: The MacMillan Co., 1961), p. 14-15.

³Stary, J., Russian J. Inorg. Chem., Eng. Trans., 4 1105 (1959).

⁴Samelson, H., Brecher, C. and Lempicki, A., J. Mol. Spect., 19(4) 349 (1966).

As Moeller⁴⁶ depicts in his review article, the gadolinium complex, for all ligands studied, is less stable than would be expected from a simple electrostatic model. There appears to be no simple explanation to clarify this "gadolinium break" although attempts have been made in terms of zero crystal-field stabilization energy and steric factors. The data for the elements studied in this work (Table 11) show the effect of this "gadolinium break" in the β_{20} and β_{30} values and also show the increase in stability as the ionic radius decreases which is well known for the lanthanides.

Dwyer and Mellor⁴⁷ list five factors that can influence the stability of metal chelates. These are:

1. The size of the chelate ring.
2. The number of rings formed by an individual molecule.
3. The basic strength of the chelating molecule.
4. Substitution of the chelating molecule which may modify basic strength or π bonding or introduce steric effects.
5. The nature of the donor or ligand atoms.

In comparing β -diketone chelates of the lanthanides, the first two and the fifth factor are held constant and any change must be due to the basic strength and/or substitution in the molecule.

⁴⁶Moeller, T., et al., Chem. Rev., 65(1) 1 (1965).

⁴⁷Dwyer, F.P. and Mellor, D.P. (ed.), "Chelating Agents and Metal Chelates" (New York: Academic Press, 1964), p. 44.

Calvin and Wilson⁴⁸ showed that, for a series of closely related chelating agents, the greater the basic strength (pK_a), the greater the stability of the metal chelate. The relation between an ion and a base is similar to that between a metal and a ligand since metal ions are Lewis acids (electron acceptors) and many ligands are the conjugate bases of acids.

The pK_a values of several β -diketones, as given by Stary,⁴⁹ are listed in Table 13. It can be seen that dipivaloyl methane has the greatest pK_a value and this, at least partially, explains the greater stability of the dipivaloyl methane complexes of the lanthanides over those of acetylacetone and benzoylacetone.

TABLE 13
 pK_a Values of Some β -diketones

<u>β-diketone</u>	<u>pK_a</u>
Acetylacetone	8.95
Benzoylacetone	8.74
Dibenzoylmethane	9.35
Dipivaloyl methane	11.76
Trifluoroacetylacetone	6.3

Van Uitert⁵⁰ has shown a correlation between $\log K_{f1}$ and $\log K_{f2}$ values for divalent metals and pK_a of several β -diketones.

⁴⁸ Calvin, M. and Wilson, K.W., J. Am. Chem. Soc., 67 2003 (1945).

⁴⁹ Stary, J., "The Solvent Extraction of Metal Chelates" (New York: Pergamon Press, 1964), p. 196.

⁵⁰ Van Uitert, J.G., Fernelius, W.C. and Douglas, B.E., J. Am. Chem. Soc., 75 2739 (1953) and 75 2736 (1953).

In general, each log value for the dibenzoylmethane complexes was more than one log unit greater than those for acetylacetone.

Van Uitert⁵¹ also found a linear relationship to be true for the Ce(III) complexes of many ligands. However, Rossotti⁵² shows the dibenzoylmethanato chelates of Ce(III) and Sc(III) are about six log units higher than for the corresponding acetylacetone complexes.

The effect of substitution on the ligand is considerably harder to evaluate due to the scarcity of information concerning β -diketones and the lanthanides. Steric effects can either increase or decrease the formation constants. In addition, substitution on the ligand can also affect the pK_a value. There is considerable evidence indicating that bulky end groups on a ligand can increase the stability of a chelate by minimizing or eliminating hydrate formation. Brown, Steinbach and Wagner⁵³ have attributed poor extraction (28% for neodymium to about 49% for terbium to about 84% for ytterbium, with pure acetylacetone) to formation of hydrates of the lanthanide chelates which are not as highly extracted as the anhydrous chelates nor as stable. They suggest that highly substituted β -diketones have additional bulky groups which sterically hinder the attachment of water to the chelate. With dipivaloyl methane, 100% is extracted for all elements studied.

⁵¹Van Uitert, L.G. and Fernelius, W.C., J. Am. Chem. Soc., 75 3862 (1953).

⁵²Rossotti, F.J.C., "Modern Coordination Chemistry", ed. Lewis, J. and Wilkins, R.G. (New York: Interscience Publishers, 1960), p. 43.

⁵³Brown, W.B., Steinbach, J.F. and Wagner, W.F., J. Inorg. Nucl. Chem., 13 119 (1960).

This indicates that the distribution ratio for the dipivaloyl methane system is higher and this is probably caused by a higher partition coefficient and/or higher stability constant, β_3 , since with dipivaloyl methane, the $[R^-]$ is much lower than with acetylacetone due to the lower DPM solubility and high pK_a value. This same concept of shielding is utilized by Van Uitert and Fernelius⁵⁴ who studied various chelates of Ce(III) and some divalent metals in 75% dioxane and found an increase in stability as the end groups were made larger. They also found that with those β -diketones having a thienyl group, the second stability constants were higher than expected and the effect is most pronounced for the third constants. Since the cerium is probably surrounded by the six atoms of the three attached β -diketones in an octahedral fashion, they reason that it would appear that the close proximity of the bulky sulfur atom to the central metal ion aids in shielding the coordination centers from interaction with the solvent.

This high stability of the dipivaloyl methane complexes can possibly be further explained in terms of the bulky end groups by a consideration of the possible entropy effect involved. Reactions in which positive ions and negative ligands interact to form complexes of lower charge proceed with a large increase in entropy; this is a major factor in the stability of the resulting complex. The large entropy change arises mainly because each charged reactant has an ordered solvation sphere. The resulting products, having a lower charge, will produce considerably less ordering of the

⁵⁴Van Uitert, L.G. and Fernelius, W.C., J. Am. Chem. Soc., 75 3862 (1953).

solvent. Sievers⁵⁵ has shown that the dipivaloyl methane chelates of the lanthanides are anhydrous and stable. Moeller⁵⁶ summarizes some evidence for the existence of $\text{Ln}(\text{H}_2\text{O})_9^3$ species. Thus in preparing the $\text{Ln}(\text{DPM})_3$ specie, there is apparently a replacement of nine H_2O by three ligands to form a stable apparently six coordinate specie. Thus there is also a possible change in coordination number which increases stability.⁵⁷

This concept of blocking of coordination sites by the bulky t-butyl groups and prevention of hydrate formation was used by Sievers in his ligand "shell" concept to explain the formation of anhydrous DPM lanthanide chelates. However, steric crowding must be considered only in relative terms as evidenced by his forming $\text{Zr}(\text{DPM})_4$. Steric factors would be expected to be more readily manifested for the association of a neutral molecule with the neutral tris complex than for an anionic ligand satisfying the charge requirements of quadrivalent zirconium. The synthesis of $\text{Zr}(\text{DPM})_4$ indicates that there is still a significant amount of room available in the tris lanthanide complexes. Thus there is room for the CH^- in the present work to satisfy the higher coordination number of the lanthanides.

The high stability of the $\text{Ln}(\text{DPM})_3$ chelates as compared to

⁵⁵Sievers, R.E., Eisentraut, K.J., Meek, D.W. and Springer, Jr., C.S., *Advances in Chemistry*, 1967, In Press.

⁵⁶Moeller, T., et al., *Chem. Rev.*, 65(1) 1 (1965).

⁵⁷Basolo, F. and Johnson, R.C., "Coordination Chemistry", (New York: W.A. Benjamin, Inc., 1964), p. 128.

the acetylacetonate or benzoylacetonate complexes is due to the much higher pK_a value of dipivaloyl methane and possibly to the steric shielding effect of the bulky t-butyl groups. The exact cause cannot be determined in this study and must await investigations such as structure, bonding and direct comparison studies.

IV Summary

It has been shown that dipivaloyl methane acts as an excellent chelating solvent for the lanthanide elements studied and extracts all of them 100% from an aqueous medium at pH values of 7 or greater. The extraction distribution data can be explained by the presence of MR_3 (R = dipivaloyl methane anion) in the organic phase and the presence of M^{+3} , MR^{+2} , either MR_2^+ or $MRCH^+$, MR_2OH , MR_3 and some species which could not be positively identified but are of a negative one and two charge. The overall stability constants for the aqueous species MR^{+2} , MR_2^+ or $MRCH^+$, MR_2OH and MR_3 and the various possible negative two species were determined. The overall extraction constant and the $P_{c\beta_3}$ values were also calculated.

APPENDIX

THE ANOMALOUS BEHAVIOR OF CERIUM

All work done on cerium, similar to that performed on the other lanthanides, led to results that were anomalous with respect to those obtained with the other lanthanides used in this study. The experimental results obtained are summarized here. Radioisotopes were used as tracers in the experimental work.

I Percent Extraction Studies

Complete extraction by a forward extraction system was never achieved. Moreover, it was not possible to account for 100% of the radioactivity. Using the procedure of dividing the organic layer radioisotope counts by the original input aqueous layer counts, the maximum extracted was about 83% and the maximum amount accounted for was about 90%. The maximum amount extracted was attained at about pH 6.6 and showed a slight decrease in percent extracted and percent accounted for to a pH ~ 8.7 and $\sim 75\%$ extraction. There was then a sharper decrease to about 37% extraction and accounted for at a pH of about 9.9. Figure 16 shows this percent extraction curve. This gives a $pH_{\frac{1}{2}}$ of 6.2 which appears to be a little low when compared with that of lanthanum ($pH_{\frac{1}{2}}$ 6.8) reported by Porell,¹ and 6.2 for praseodymium

¹Porell, A.L., Private Communication.

FIGURE 16

Percent Extraction of Cerium
as a Function of pH

reported in this work. This work was done on 2.5×10^{-5} M Ce^{+3} solution. Work done on 2.5×10^{-3} M solutions indicated the presence of an insoluble orange film forming at the interface between the two phases. Attempts to recover this film for analysis by filtration techniques were unsuccessful. This film was not formed when using 2.5×10^{-3} M Ce^{+3} in a back extraction procedure.

The above procedures were done in the presence of dilute $\text{NH}_2\text{OH}\cdot\text{HCl}$ in the stock bottle and N_2 was bubbled through the ten ml aqueous phase and five ml organic phase for five to ten minutes before mixing. This procedure was designed to eliminate or at least to minimize any chance of the cerous hydroxide being oxidized to ceric hydroxide in basic media.²

Using 2.5×10^{-3} M Ce^{+3} to produce a visible precipitate, it was observed that where the above precautions were followed, the blue white gelatinous precipitate of $\text{Ce}(\text{OH})_3$ was produced which did not turn color on shaking or standing for several days. However, if the above precautions were not taken, a reddish gelatinous precipitate was formed which would not extract. This precipitate is probably an insoluble peroxide or hyperoxide since $\text{Ce}(\text{OH})_4$ is a yellowish precipitate. Attempts were made to extract Ce^{+4} without any success as neither the $\text{Ce}(\text{OH})_4$ nor this reddish precipitate would extract at all with pure dipivaloyl methane whereas the $\text{Ce}(\text{OH})_3$ would, within the limitations listed above.

²Kolthoff, I.M. and Elving, P.S., "Treatise on Analytical Chemistry" (New York: John Wiley and Sons, Inc., 1963), Part II, Vol. 8, p.

II Distribution Studies

Since 85% of the cerium could be extracted in the forward procedure and since there is no concentration dependence below 10^{-4} M concentration, it was deemed possible to do a distribution study by the back extraction procedure. This procedure was used on the 2.5×10^{-5} M Ce^{+3} solutions and it was found that the log D vs pH curve was similar to that obtained for the other lanthanides studied at pH values greater than about 9 but below that, there was a leveling out of D values all the way down to pH $\approx$ 2. See Figure 17. The data showed much more scatter than that of the other lanthanides. It was found necessary to use a 10% acid solution to completely remove the color and completely extract the cerium back into the aqueous phase. Apparently a very strong chelate is formed.

III Separation of Cerium from Other Lanthanides

Several attempts were made to separate cerium from the remainder of the lanthanides utilizing the fact that Ce(IV) could not be extracted. Attempts at gross precipitation and precipitation from homogeneous solutions all proved unsuccessful which is not surprising considering the well-known affinity of the lanthanides for co-precipitating with each other.³ Some of these attempts were:

- a) Oxidizing Ce(III) to Ce(IV) in acid solution and

³Stevenson, P.C. and Nervi, W.E., "The Radiochemistry of Scandium, Yttrium and the Rare Earths" (National Academy of Science, National Science Foundation, 1961), p. 29.

FIGURE 17

Distribution Curve for Cerium
as a Function of pH

adjusting the pH to 4 at which point $\text{Ce}(\text{OH})_4$ should precipitate and the trivalent lanthanides should remain in solution. Europium or gadolinium in concentrations of 10^{-3} M and 10^{-5} M were mixed with 10^{-3} and 10^{-5} M Ce solutions and it was found that the europium or gadolinium activity had co-precipitated with the $\text{Ce}(\text{OH})_4$.

b) Precipitating Ce(III) and Eu(III) hydroxides at pH 9 - 10 and oxidizing the cerium with H_2O_2 . Again it was found that most of the europium activity was with the insoluble cerium although a small amount was extracted along with some cerium.

c) Making the solution containing Ce(III) and Gd(III) acid, oxidizing the Ce(III) using $\text{K}_2\text{S}_2\text{O}_8$, and attempting precipitation from homogeneous solution of the $\text{Ce}(\text{OH})_4$ by heating with urea. Again practically all of the gadolinium was found with the cerium precipitate.

d) Oxidizing the Ce(III) in the cerium-gadolinium solution in an acid solution, using $\text{K}_2\text{S}_2\text{O}_8$, adding KIO_3 and digesting on a steam bath for about two hours until the $\text{Ce}(\text{IO}_3)_4$ became crystalline. Again co-precipitation was essentially complete and little gadolinium was found in the organic phase.

A mixture of europium and cerium (III) was adjusted to pH 9 and both extracted into the organic phase. The organic phase was then shaken with an aqueous phase of 0.1 M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ at pH 3.5. All of the europium was then back-extracted into the aqueous phase while essentially all of the cerium remained in the organic

adjusting the pH to 4 at which point $\text{Ce}(\text{OH})_4$ should precipitate and the trivalent lanthanides should remain in solution. Europium or gadolinium in concentrations of 10^{-3} M and 10^{-5} M were mixed with 10^{-3} and 10^{-5} M Ce solutions and it was found that the europium or gadolinium activity had co-precipitated with the $\text{Ce}(\text{OH})_4$.

b) Precipitating $\text{Ce}(\text{III})$ and $\text{Eu}(\text{III})$ hydroxides at pH 9 - 10 and oxidizing the cerium with H_2O_2 . Again it was found that most of the europium activity was with the insoluble cerium although a small amount was extracted along with some cerium.

c) Making the solution containing $\text{Ce}(\text{III})$ and $\text{Gd}(\text{III})$ acid, oxidizing the $\text{Ce}(\text{III})$ using $\text{K}_2\text{S}_2\text{O}_8$, and attempting precipitation from homogeneous solution of the $\text{Ce}(\text{OH})_4$ by heating with urea. Again practically all of the gadolinium was found with the cerium precipitate.

d) Oxidizing the $\text{Ce}(\text{III})$ in the cerium-gadolinium solution in an acid solution, using $\text{K}_2\text{S}_2\text{O}_8$, adding KIO_3 and digesting on a steam bath for about two hours until the $\text{Ce}(\text{IO}_3)_4$ became crystalline. Again co-precipitation was essentially complete and little gadolinium was found in the organic phase.

A mixture of europium and cerium (III) was adjusted to pH 9 and both extracted into the organic phase. The organic phase was then shaken with an aqueous phase of 0.1 M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ at pH 3.5. All of the europium was then back-extracted into the aqueous phase while essentially all of the cerium remained in the organic

phase, as shown in Table 14. However, due to the inability to achieve 100% extraction of cerium in the forward extraction, this procedure would not be suitable for separation and determination of cerium but could be used for the elimination of cerium impurities from europium and probably from any mixture of the lanthanides.

TABLE 14
Separation of Cerium from Europium

Concentration in initial aqueous phase	Cerium 2.5×10^{-5} M	Europium 2.5×10^{-5} M
% extracted into organic phase	81%	99.9%
% of organic phase back- extracted into aqueous phase Equil. pH 3.5	< 0.1 %	> 99.9%

BIBLIOGRAPHY

Books

- Basolo, F. and Johnson, F.C. "Coordination Chemistry". New York: W.A. Benjamin, 1964.
- Cheronis, N.D. and Entrikin, J.B. "Semimicro Qualitative Organic Analysis". New York: Thomas Y. Crowell Co., 1947.
- Dwyer, F.P. and Mellor, D.P. (ed.). "Chelating Agents and Metal Chelates". New York: Academic Press, 1964.
- Grenthe, I. and Fernelius, W.C. "Rare Earth Research". Edited by Eugene V. Kleber. New York: MacMillan Co., 1961.
- Kolthoff, I.M. and Elving, P.S. (ed.). "Treatise on Analytical Chemistry". Part II, Vol. 8. New York: Interscience Publishers, John Wiley and Sons, Inc., 1963.
- Larsen, E.M. "Transitional Elements". New York: W.A. Benjamin, 1965.
- Morrison, G.H. and Freiser, H. "Solvent Extraction in Analytical Chemistry". New York: John Wiley and Sons, Inc., 1957.
- Peppard, T. and Mason, G.W. "Rare Earth Research". Edited by Eugene V. Kleber. New York: MacMillan Co., 1961.
- Rao, C.N.R. "Ultra-Violet and Visible Spectroscopy". London: Butterworth's, 1961.
- Rossotti, F.J.C. and Rossotti, H. "Determination of Stability Constants". New York: McGraw Hill, 1961.
- Rossotti, F.J.C. "Modern Coordination Chemistry". Edited by J. Lewis and R.G. Wilkins. New York: Interscience Publishers, 1960.
- Schweitzer, G.K. and VanWillis, W. "Advances in Analytical Chemistry and Instrumentation". Vol. V. New York: John Wiley and Sons, Inc., 1966.

Scott. "Standard Method of Chemical Analysis". Edited by N.H. Furman. New York: D. VanNostrand Co., Inc., 1939.

Sievers, R.E. and Mosher, R.W. "Gas Chromatography of Metal Chelates". New York: Pergamon Press, 1965.

Stary, J. "The Solvent Extraction of Metal Chelates". New York: Pergamon Press, 1964.

Stevenson, P.C. and Nervik, W.E. "The Radiochemistry of Scandium Yttrium and the Rare Earths". National Academy of Science, National Science Foundation, 1961.

Journals

Bauer, H., Blanc, J. and Ross, D.L. J. Am. Chem. Soc. 86 5125 (1964).

Brown, W.B., Pope, G.W., Steinbach, J.F. and Wagner, W.F. J. Inorg. Nucl. Chem. 25 429 (1963).

Brown, W.B., Steinbach, J.F. and Wagner, W.F. J. Inorg. Nucl. Chem. 13 119 (1960).

Calvin, M. and Wilson, K.W. J. Am. Chem. Soc. 67 2003 (1945).

Connick, R.E. and McVey, W.H. J. Am. Chem. Soc. 71 3182 (1949).

Dyrssen, D. Svensk. Kemisk. Tidskrift. 68 212 (1956).

Dyrssen, D. and Sillen, L.G. Acta Chem. Scand. 7 663 (1953).

Eisentraut, K. and Sievers, R.E. J. Am. Chem. Soc. 87 5254 (1965).

Guter, G.A. and Hammond, G.S. J. Am. Chem. Soc. 78 5166 (1956).

_____. J. Am. Chem. Soc. 81 4686 (1959).

Halverson, F. Brinen, J. S. and Leto, J.R. J. Chem. Phys. 40 2790 (1964).

Hammond, G.S., Bordium, W.G. and Guter, G.A. J. Am. Chem. Soc. 81 4682 (1959).

Hammond, G.S., Nonhebel, D.C. and Wu, C.S. Inorg. Chem. 2 73-76 (1963).

Izatt, R.M., Fernelius, W.C., Haas, Jr., C.G. and Block, B.P. J. Phys. Chem. 59 170 (1955).

- Keenan, T.K. and Suttle, J.F. J. Am. Chem. Soc. 76 2184 (1954).
- Khomenko, V.S. and Kuznetzova, V.V. Doklady Akad. Nauk. Belorussk. S.S.R. 9 610 (1963).
- Krishen, A. and Freiser, H. Anal. Chem. 37 923 (1959).
- Linn, B.O. and Hauser, C.R. J. Am. Chem. Soc. 78 6066 (1956).
- Man, E.H., Swamer, F.W. and Hauser, C.R. J. Am. Chem. Soc. 73 901 (1951).
- Melby, L.R., Rose, N.J., Abramson, E. and Caris, J.C. J. Am. Chem. Soc. 86 5117 (1964).
- Moeller, T. J. Phys. Chem. 50 242 (1946).
- Moeller, T., et al. Chemical Reviews. 65(1) 1 (1965).
- Morie, G.P. and Sweet, T.R. Anal. Chim. Acta. 34 314 (1966).
- Morrison, G.W. and Freiser, H. Anal. Chem. 38 131R (1966).
- _____. Anal. Chem. 36 93R (1964).
- _____. Anal. Chem. 30 632 (1958).
- Panova, M.G., Levin, V.I. and Brezhneva, N.E. Radiochemistry, USSR. Vol. II, No. 2 209 (1960).
- Pope, G.W. Steinbach, J.F. and Wagner, W.F. J. Inorg. Nucl. Chem. 20 304 (1961).
- Poskanzer, A.M. and Foreman, Jr., B.M. J. Inorg. Nucl. Chem. 16 323 (1961).
- Ruzicka, J. and Stary, J. Talanta. 10 287-293 (1963).
- Rydberg, J. Acta Chem. Scand. 4 1503 (1950).
- _____. Acta Chem. Scand. 14(1) 157 (1960).
- _____. Arkiv. Kemi. 8 101 (1955).
- _____. Rec. Trav. Chim. 75 737 (1956).
- Samelson, H., Brecher, C. and Lempicki, A. J. Mol. Spect. 19(4) 349 (1966).
- Schweitzer, G.K. and VanWillis, W. Anal. Chim. Acta. 36 77-89 (1966).
- Sievers, R.E., Eisentraut, K.J., Meek, D.W. and Springer, Jr., C.S. Advances in Chemistry, In Press, 1967.

- Stary, J. Anal. Chim. Acta. 28 132 (1963).
- _____. Russian J. Inorg. Chem., Eng. Trans. 4 1105 (1959).
- Stary, J. and Hladky, E. Anal. Chim. Acta. 28 227 (1963).
- Steinbach, J.F. and Freiser, H. Anal. Chem. 26(6) 881 (1953).
- Sullivan, J.C., Rydberg, J. and Miller, W.F. Acta Chim. Scand. 13(10) 2023 (1959).
- Tobias, R.S. and Garrett, A.B. J. Am. Chem. Soc. 80 3532 (1958).
- Van Uitert, L.G. and Fernelius, W.C. J. Am. Chem. Soc. 75 3862 (1953).
- _____, J. Am. Chem. Soc. 75 2739 (1953).
- _____. J. Am. Chem. Soc. 75 2736 (1953).
- Wagner, W.F. Record of Chem. Prog. 23(3) 155 (1962).

Other Sources

- Morie, G.P. Ph.D. Dissertation. The Ohio State University, 1966..