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LANTHANIDE EXTRACTION WITH 2,5-DIMETHYL-2-HYDROXYHEXANOIC ACID

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Lanthanide extraction with
2,5-dimethyl-2-hydroxyhexanoic acid*

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This research is concerned with the solvent extraction into chloroform of the lanthanides, using 2,5-dimethyl-2-hydroxyhexanoic acid (DMHHA). This acid is the first α-hydroxy aliphatic acid to be studied as an extracting agent for the lanthanides.

The chloroform-water DMHHA partition constant was determined to be 1.0 (at 0.1 M ionic strength and 25°C). The acid dimerizes in chloroform with a constant of 56.

The light lanthanides can be extracted into chloroform by forming complexes with the DMHHA anions. The extracted metal species is highly aggregated. This extraction has a solubility limit which increases with the addition of unionized acid. The resultant extract is also highly

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aggregated. At unionized acid-to-metal ratios greater than one, extractions first occur followed by the slow precipitation of the lanthanide.

At the tracer level, neodymium is extracted primarily as $NdA_3(HA)_5$ and $(NdA_3)_2(HA)_q$. Very small amounts of $(NdA_3)_2$ and other metal aggregates are also present.

The heavy lanthanides do not extract from solutions of DMHHA and its potassium salt, but form aqueous emulsions and precipitates. In the presence of the organic soluble tetrabutylammonium ion the heavy lanthanides can be extracted, presumably as ion pairs.

The stability constants of the light lanthanides and DMHHA were determined. The separation factors obtained from DMHHA extractions of the light lanthanides were also investigated and found to be comparable to those obtained employing normal aliphatic carboxylic acids.

I. INTRODUCTION

Many extracting agents have been examined as potential agents for the solvent extraction separation of the lanthanides. Particular interest has been generated in the area of nuclear waste processing. Carboxylic acids are one group of extracting agents which have been the subject of several studies, but the separation factors obtained from such investigations have not been as favorable as those reported for other extractants. The α-hydroxy carboxylic acids, which might be expected to show improved selectivity, have yet to be examined.

This dissertation is concerned with the solvent extraction of lanthanides into chloroform using 2,5-dimethyl-2-hydroxyhexanoic acid. Special attention is devoted to identifying the species which extract. Both macroscopic and tracer-scale extractions are discussed, and separation factors for the extraction of the light lanthanide pairs are reported. The acid anion protonation constant, the acid chloroform-water partition constant and the acid dimerization constant in chloroform are also reported.

II. LANTHANIDE EXTRACTIONS

A variety of extracting agents have been investigated for use in the solvent extraction separation of the rare earths. These agents can be roughly placed into the following classifications: 1) neutral phosphates, 2) acidic phosphates, 3) amines, 4) carboxylic acids, and 5) other. Extracting agents from all of these groups will be discussed in this chapter, with the exception of the carboxylic acids, which will be discussed in greater detail in the following chapter.

A significant portion of the work in the area of lanthanide extraction has been fostered by an interest in nuclear waste processing. For safety reasons, there is a desire to separate the transplutonium elements, chiefly americium and curium, from nuclear wastes already depleted in uranium and plutonium. Unfortunately, about one-third by weight of these waste products are lanthanides, which have very similar chemical properties to the heavier actinides. This difficult actinide/lanthanide separation is one of major active interest. For this reason this chapter, in addition to reviewing lanthanide extractions, will discuss some of the more pertinent applications to nuclear waste processing.

As an aid to understanding the following material, a few preliminary definitions are presented:

extracting agent (EA), is the compound that interacts with the substance in solution to cause its extraction.

extractant, is the liquid phase that extracts. It may be an extracting agent by itself or in the presence of a diluent.

extract, is the phase containing the extracted substance.

extracted species, is the particular form in which the extracted substance is found. More than one extracted species may be formed in the extract.

distribution ratio (D), is the ratio of the total equilibrium concentration of all forms of the substance in the extract to total equilibrium concentration of all forms in the aqueous phase.

atomic number is represented by z.

A. Neutral Phosphorus Agents

Tributylphosphate (TBP) has been one of the most thoroughly studied extracting agents for the lanthanides. The extraction mechanism can be represented as follows:

$$(Ln^{3+})_a + 3(X^-)_a + n(TBP)_o \rightleftarrows (LnX_3 \cdot nTBP)_o$$

where $X^- = NO_3^-$, Cl^-, ClO_4^-, and n is usually 3. Generally, the extraction is best from an aqueous solution of high acidity and high salt concentration. Since the order of extractability and selectivity are parallel ($NO_3^- > Cl^- > ClO_4^-$) (1), nitrate solutions are usually employed.

The dependence of the distribution ratio on aqueous acidity is not regular (2). D generally increases to a maximum at concentrations around 3 - 5 M HNO_3, then falls slightly before increasing rapidly at higher acidities. Both the amount of downward inflection and the acidity of the subsequent rise, decrease with an increase in z. At low acidities (<5 M HNO_3), D increases with z until Gd, after which it steadily falls. This fall has been attributed to a decreased electrostatic interaction between the hydrated cation and the anion. At higher acidities the distribution coefficient generally increases with z (3).

The separation factors observed for adjacent rare earths extracted with TBP are not very good, and certainly inferior to those obtained with other systems. However, the light lanthanides can be partitioned from the trivalent actinides and heavy lanthanides using a high concentration of a salting agent such as $Al(NO_3)_3$ (4,5). From a nuclear waste standpoint this may prove useful for a preliminary separation of the actinides. Coextraction of zirconium could be a problem (5). Also, the selectivity obtained is still less than desirable, and an additional process would be needed to achieve the desired separations. Other phosphates have been studied but offer no advantages over TBP (6).

Another group of neutral extracting agents which have been investigated are the phosphonate esters, compounds with one of the alkyl or aryl groups directly attached to the phosphorus. Diisopentyl methylphosphonate has been found to extract at lower salt concentrations than TBP, and to give better D's and S.F.'s (7-9). Dibutyl butylphosphonate has also been suggested as a superior extracting agent (10).

Trialkylphosphine oxides have also been examined as potential EA's for the lanthanides. Trioctylphosphine oxide has been the subject of a number of studies. Due to its improved selectivity over TBP, it could find use in nuclear waste partitioning (5). It apparently has no value for lanthanide separations (6). Extractions with triisopentylphosphine oxide show higher D's and S.F.'s than either TBP or the phosphonates. As with TBP, the distribution coefficients increase with z until the middle of the series and then fall (11).

Some related nonphosphorus containing nitrogen and sulfur oxides have been found to extract the lanthanides as anhydrous trisolvates (7). For EA's in the same class of compounds, the extracting strength and selectivity were found to change in parallel. In another study (12), extraction with dialkyl sulfoxides produced highly hydrated trisolvates. The distribution constants obtained were rather low.

B. Acidic Phosphorus Agents

Di(2-ethylhexyl)phosphoric acid (HDEHP) has been the subject of numerous studies. It is readily available, has a low aqueous solubility, and because of its high viscosity, is usually used with a diluent. Lanthanide extraction proceeds via the following reaction (13),

$$Ln^{3+}_{aq} + 3(HDHEP)_{2,org} \rightleftarrows Ln(H(DEHP)_2)_{3,org} + 3H^{+}_{aq}$$

which holds at low concentrations of salt and mineral acid. At higher acidities partial anion coextraction occurs, which lowers the separation factors (14,15). The formation of polymeric extracted species is observed at higher lanthanide salt concentrations (16,17).

Unlike TBP, the HDEHP-lanthanide distribution coefficients increase regularly with z, yielding very favorable separation factors. The diluent used can show a profound influence on the distributions obtained (18,19). As a rule, D decreases with an increase in the polarity of the diluent, apparently due to suppressed formation of the extractable complex.

HDEHP is a good extractant for both lanthanides and actinides and is used in the TALSPEAK process for partitioning the transplutonium actinides from nuclear waste (20,21). The TALSPEAK process evolved from the HDEHP extraction of lanthanides and actinides from an aqueous phase containing a carboxylic acid (usually lactic) and a complexing agent such as DTPA. The actinides were extracted about 1/10th as much as the least extractable lanthanides, those in the middle of the series.

In a German adaptation (22) of this process, the acidity of the waste stream is first reduced by decomposition of HNO_3 with formic acid, followed by the addition of lactic acid and extraction with HDEHP. The lactic acid is added to prevent coextraction of zirconium and iron. The actinides and lanthanides are both removed and partitioned by back-extraction into a sodium DTPA solution. A similar Russian process (23) uses sodium acetate and citrate to adjust the pH. Though the TALSPEAK method is presently the best partitioning method available, it suffers from drawbacks (24) which make further extraction studies desirable.

A number of other dialkyl phosphoric acids, HO(RO)(R'O)PO, have been examined as potential EA's for the lanthanides (25). Branching of the alkyl groups has been found to decrease the D's obtained, but to have little effect on the separation factors. The temperature dependence of lanthanide extractions with dialkyl phosphoric acids, is not regular (26). With an increase in temperature, improved S.F.'s through about Nd are seen, after which the separation factors are lowered. Dibutyl phosphoric acid offers improved selectivity over HDEHP for the heavy lanthanides, but inferior selectivity with the light lanthanides.

As with the neutral phosphates, the monoacidic phosphates can have one or both alkyl groups directly bonded to the phosphorus. The former are phosphonates, the most widely studied one being ethylhexylphenylphosphonic acid. Like the other phosphonates, it is a stronger EA than the monoacidic phosphates (6,26). Its lanthanide separation factors are better than those of HDEHP, but problems with the coextraction of other metals has prevented its use in waste reprocessing (27).

Monoacidic phosphinates are also strong extracting agents. The dependence of D on the phosphinic acid concentration has been found to vary between 2.2 and 3, and may suggest a mixture of complex species (28,29). In experiments using diphenylphosphinic acid (HY) in $CHCl_3$, a number of extracted species were formed: $MY_n(HY_2)_{3-n}$ n = 0-3 (30). The nondimerized ligands were visualized as binding bidently, perhaps with the incorporation of water molecules into the chelate ring.

C. Amine Extracting Agents

A variety of amines have been used in the extraction of lanthanides. The extraction mechanism is one of anion exchange. Using a tertiary amine and a univalent anion, it can be represented as

$$(n-3)(R_3NH^+ \ldots X^-)_{org} + MX_{n,aq}^{-(n-3)}$$

$$\rightleftarrows ((R_3NH^+)_{n-3} \ldots MX_n^{-(n-3)})_{org} + (n-3)\ X^-_{aq}$$

where n is usually 4 or 5. In extractions involving divalent anions, ion pairs with 3 to 5 cations have been reported (31,32). When the anion is SCN^-, the D's steadily increase with z. With NO_3^- the opposite trend is observed. This decreased extractability with z has been attributed to the increased hydration sheath of the predominately outer-sphere nitrate complexes (33).

Lanthanide extractions using either primary or secondary amines generally need either high salt or acid concentrations to be efficient. The aqueous solubility of many primary amines is too large for practical applications. Primene-JM-T extractions from sulfate solutions seem to give the best results (34).

Tertiary amine extractions also require high acid or salt concentrations to produce significant partitioning. The methyldi-n-octyl and methyldi-n-heptyl amines show higher selectivities than the symmetrical tertiary amines (35,36). This has been attributed to a difference in the extracting species, which is apparently controlled by steric factors. There seems to be no clear correlation between amine basicity and extractant strength.

Triisooctylamine hydrochloride has shown good selectivity between the actinides and the lanthanides in extractions from highly salted LiCl solutions (37). The similar tricaprylylamine (Alamine 336), forms the basis for the TRAMEX process, which separates the actinides from the lanthanides. The amine hydrochloride is used with a diethylbenzene diluent (38). Extraction takes place from 11 N LiCl, which may cause corrosion problems in nuclear process applications. This high amount of salt would need to be recycled for it would otherwise increase nuclear waste disposal problems (5,24).

The quaternary amine salt, methyltricaprylyl ammonium thiocyanate (Aliquat 336-Cl) has been found to offer advantages over other amines in An/Ln extractions. Though the separation factors are good, SCN^- decomposition and occasional organic phase aggregation (19) preclude its use in waste reprocessing. The related cetyl pyridinium lanthanide salts also show aggregation in $CHCl_3$ extractions (39). It is possible that similar aggregation of the extracted species may account for the behavior observed in other amine extractions where a mixture of nonaggregated species has been proposed (36).

D. Other Extracting Agents

Of the other extracting agents studied, the β-diketones have received the most attention. Acetylacetone will extract individual lanthanides up to a solubility maximum (40), though hydrolysis is a problem because of the high pH needed for extraction (41). Fluorinating one methyl group and substituting for the other methyl group on acetylacetone gives β-diketones which are more acidic and which form more soluble salts. Of the substituted diketones 2-thenoyltrifluoroacetone (HTTA) has been the most popular. It extracts via the following mechanism (42):

$$Ln^{3+}{}_{aq} + 3(HTTA)_{org} \rightleftarrows (Ln(TTA)_3)_{org} + 3H^{+}{}_{aq}$$

The extraction is considerably enhanced in the presence of an acetate buffer. In general, β-diketones have not found any practical separation application due to their slow kinetics, weak extraction capacity and lack of stability (43). The similar extracting agent 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone appears to be definitely superior (44). In experiments with several alcoholic diluents, complete europium extraction was achieved in the pH 1-2 range.

Of the readily available alcohols, ethers, esters and ketones, only diethyl ether and 2-pentanone extract the lighter lanthanides to any degree. Neither has particular value for separations work. Hydroxamic acids can serve as extracting agents, but because of their low pK's, extract only at high pH values. Cupferron and the hydroxyquinolines also extract at pH > 6.

III. CARBOXYLIC ACID LANTHANIDE EXTRACTION

This chapter is divided into two sections. The first section concerns itself with the mechanisms and equilibria involved in extractions using carboxylic acids. The second section reviews lanthanide carboxylate extractions in detail. Some of the equilibria discussed in the first section have been employed in the evaluation of such extractions.

A. Extraction Equilibria

Extraction of metals by carboxylic acids involves the formation of metal carboxylates and can be represented by:

$$(M^{x+})_a + x(HA)_o \rightleftarrows (MA_x)_o + x(H^+)_a \qquad (1)$$

where the subscripts a and o denote the aqueous and organic phases, respectively. The pH dependence of this reaction is utilized in separations work, wherein selectivity is regulated by accurate pH control.

Unless the x carboxylate anions completely satisfy the metal coordination requirements by properly chelating, additional unionized acid species may react to fill the coordination sphere:

$$(M^{x+})_a + (x+n)(HA)_o \overset{K_{eq}}{\rightleftarrows} (MA_x(HA)_n)_o + x(H^+)_a \qquad (2)$$

The values of x and n are obtained experimentally by measuring the distribution coefficient

$$\left(D = \frac{\Sigma \text{ metal in organic phase}}{\Sigma \text{ metal in aqueous phase}}\right)$$

under a variety of conditions. If one assumes that M^{x+} is the only metal-containing species in the aqueous phase and $MA_x(HA)_n$ is the only species in the organic phase, then

$$D = \frac{[MA_x(HA)_n]}{[M^{x+}]} \ .$$

By substituting this into equation 2 and taking the logarithm of each side, the following expression is obtained:

$$\log D = \log K_{eq} + (n+x) \log [HA]_o - x \log [H^+] \qquad (3)$$

The value of x is usually obtained by plotting log D against pH at constant $[HA]_o$. The value of n is then determined by plotting log D *vs* log $[HA]_o$ at a constant pH.

Since the individual activities are not known, they are replaced by concentrations and the equilibrium constant is appropriately modified (equation 4). Activity effects

$$K_{eq'} = K_{eq} \frac{(\gamma^{\pm}_{M^{x+}})(\gamma_{HA})^{n+x}}{(\gamma^{\pm}_{H^+})^{x}(\gamma_{MA_x(HA)_n})} \qquad (4)$$

can be kept to a minimum by working at constant ionic strength, though even then, they place obvious limitations on accuracy and validity.

Occasionally, $[HA]_o$ is measured directly, but it is frequently assumed to equal the initial acid concentration in the organic phase. This assumption is not valid if: 1) the acid is appreciably soluble in the aqueous phase; 2) the acid dimerizes in the organic phase; or 3) the initial metal concentration is of the same order of magnitude as the organic acid concentration. Conditions 1 and 2, if extant, can be accounted for by considering the following equilibria,

$$K_{D,O} = [H_2A_2]_o/[HA]_o^2 \qquad P_{HA} = [HA]_o/[HA]_a$$

where the values of $K_{D,O}$ and P_{HA} have been determined from experiments in the absence of metal. $[HA]_o$ can then be calculated. Condition 3 is usually avoided by working at tracer-level metal concentrations or at very high $[HA]_o$ concentrations.

Frequently, more than one metal species is present in the aqueous phase, and these must be taken into consideration:

$$\text{Total aq. metal} = [M^{x+}] + [MA^{(x-1)+}] + \ldots + [MA_x]$$

$$C_{m,a} = [M^{x+}] + \beta_1[M^{x+}][A^-] + \ldots + \beta_x[M^{x+}][A^-]^x$$

$$= [M^{x+}] \cdot (1 + \beta_1[A^-] + \beta_2[A^-]^2 + \ldots + \beta_x[A^-]^x) \qquad (5)$$

The β's can be determined by separate experiments (45). Incorporation of the above into the equation 3 yields

$$\log D = \log K_{eq'} + (n+x) \log [HA]_o - x \log [H^+]_a - \log (\sum_o^x \beta_x[A^-]_a^x) \qquad (6)$$

Further complications arise if the extracted species is aggregated:

$$J(M^{x+})_a + (J \cdot x+n)(HA)_o \rightleftarrows ((MA_x)_J(HA)_n)_o + J \cdot x(H^+)_a \qquad (7)$$

When the value of x obtained from a log D vs pH plot is larger than the charge on the metal ion, this may indicate polymer formation. A plot of D vs $[M^{x+}]_a$ will provide more information. A positive slope is indicative of aggregate formation, while a steadily decreasing D can be attributed to a variety of factors. Aqueous phase hydrolysis, overlooked aqueous complexation, organic phase solubity saturation, and aqueous polymerization all may produce such behavior.

The extraction of a single aggregated species $(MA_x)_J(HA)_n$ yields the following expression:

$$K_{eq'} = D[M^{x+}]_a^{1-J} \cdot \frac{1}{J} \cdot [H^+]^{xJ} \cdot (\sum_{o}^{x} \beta_x [A^-]_a^x) \cdot (Jx+n)[HA]_o$$

from which the appropriate log-log plots can be developed. The presence of a number of aggregated species invalidates graphical treatment using log plots and makes analyses extremely difficult.

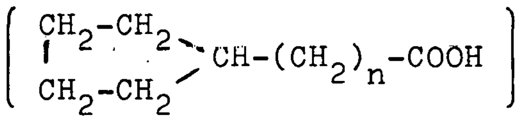
Two other methods have been used to determine the nature of the extracting species. The first is the method of isomolar series (continuous variations) which has also found frequent application in work on homogeneous solutions. As applied to extraction, the method consists of varying the proportions of two reacting species while keeping the sum of the two concentrations constant and measuring the amount of extraction. For the method to be applicable, only one complex can be extracted. This isomolar series method also has limited value in systems where stepwise complexes are formed (46).

The other method is the method of molar ratios. In this method the amount of one component is held constant while the other is varied, and the amount of subsequent extraction measured. Though useful for simple systems, the molar ratio method suffers from similar drawbacks as those inherent in the isomolar series method.

B. Extraction of Lanthanides

In the previous chapter, a variety of extracting agents for the lanthanides was reviewed. A few types of agents have been studied in great detail. In contrast, carboxylic acids have not received much attention, though interest in them has been increasing in recent years.

Because of their low cost and availability as petroleum by-products, naphthenic acids



have been the subject of several studies. In lanthanide extractions using hexanol and diethyl ether as diluents, Bauer and Lindstrom (47) found D to increase with either an increase in acid concentration or pH. At a pH of 6, an acid to metal ratio of over 17 was needed to effect quantitative extraction. The heavy lanthanides were more extractable, but the individual separation factors were poor.

Alekperov and Geibatova (48) studied lanthanide extraction into kerosene-diluted naphthenic acids. The pH of 50% extraction ($pH_{\frac{1}{2}}$) was found to decrease through Gd and then to steadily increase. A nonlinear dependence of log D on log $C_{m,a}$ suggested possible aggregation of the extract. The expected value of 3 was obtained from a plot of log D versus pH. The individual separation factors were very small.

In further work with neodymium, Mikhlin et al. (49) confirmed the x value of 3, and found the solvate number n to also equal 3. From a plot of $pH_{½}$ vs $C_{m,a}$, the extracted species was determined to be dimeric, $(NdA_3(HA)_3)_2$, in the salt concentration range 0.01 - 0.1 M.

In contrast, Korpusov et al. (50), with a concentration in heptane of less than 3×10^{-3} M, determined the extracting species to be strictly monomeric. Separation factors were again poor, but increased with the introduction of salting-out agents such as $LiNO_3$. Use of EDTA or DTPA as an aqueous phase complexing agent retards the extraction of the heavier lanthanides and one or the other may find some separations application.

Plaksin et al. (51-52) studied the effect of the solvent on extractions with C_7-C_9 mixtures of carboxylic acids. The $pH_{½}$ was found to increase with an increase in polarity: kerosene < CCl_4 < m-xylene < isoamyl acetate < decanol < hexanol. A mixture of C_7-C_9 acids was also used in extractions by Korpusov et al. (53), since acids of lower molecular weight are too water soluble, and lanthanide salts of higher carboxylic acids show reduced organic phase solubility. The cerium subgroup, and cerium in particular, formed the most soluble salts. The separation factors observed were rather poor, but improved with the addition of a salting-out agent. This improvement was attributed to a favorable change in the ratio of the aqueous lanthanide activity coefficients. Good separations of the light lanthanides were obtained by adding NTA to the aqueous phase. Although the extraction selectivity is poor in the presence of C_7-C_9 acids alone, NTA complexes the heavier lanthanides to a greater extent and the lighter elements are selectively extracted.

Schweitzer and Sanghvi (54) examined tracer-level thulium extractions with formic through decanoic acids. Extraction steadily increased from butyric through hexanoic acid and then marginally increased through decanoic acid. In further studies with hexanoic acid, the species extracting into $CHCl_3$ and 4-methyl-2-pentanone were determined to be $TmA_3(HA)_5$ and $TmA_3(HA)$, respectively. In the latter, the ketone probably helps to solvate the complex. Comparison of log D versus pH plots at differing metal concentrations, suggested no polymerization at metal salt concentrations less than 10^{-4} M.

Norina et al. (55) measured lanthanide extractions from highly salted solutions by a variety of normal carboxylic acids. In contrast to the preceding work, these authors found the extraction to decrease with an increase in the number of carbons in the carboxylic acid.

In a series of papers Korpusov et al. (56) and Danilov et al. (57,58) have reported on extractions using α,α-disubstituted carboxylic acids, usually containing eight or nine carbons. For two acids, the organic phase dimerization constant and the acid partition constant were obtained in several solvents. With an increase in solvent polarity, $K_{D,O}$ decreased and P_{HA} increased. Applying these constants in analyzing lanthanide extractions, the extracting species were all found to be $LnA_3(HA)_3 \cdot yH_2O$. The hydrate number varied between one and two, but approached one at increasing lanthanide salt concentrations. At salt concentrations greater than 10^{-3} M, the extracting species may be aggregated. For lanthanide separations, these α,α-disubstituted carboxylic acids showed better selectivity than either the naphthenic or normal carboxylic acids.

The selectivity and extraction efficiency of a number of carboxylic acids have been noted by Mikhailichenko et al. (59). The degree of lanthanide extraction was found to decrease in the order n-RCOOH > β-RCOOH > α-RCOOH > α,α-RCOOH. The separation factors increased in the opposite order. This increase in selectivity with branching of the acid was attributed to a greater rearrangement of the lanthanide solvent sheath, caused by the larger volume substituent in the α position. This viewpoint was supported by the reported decrease in hydration of the extracted species in going from an unbranched to an α,α-branched extracting agent.

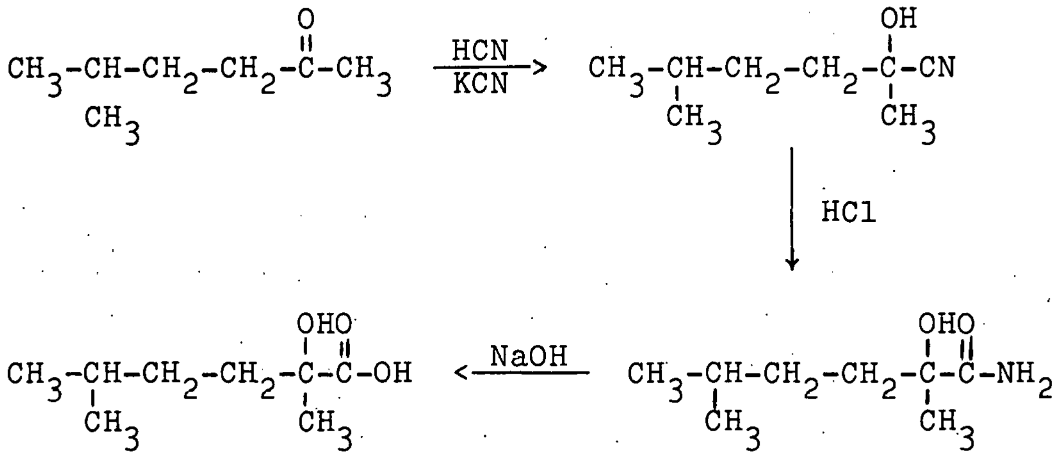
As a rule, however, all of the carboxylic acids studied have shown either low selectivity or selectivity limited to a group of lanthanides. The best separations are obtained when using aqueous complexing agents in conjunction with carboxylic acid extractants. Hydroxycarboxylic acids, which might offer better selectivity towards extraction, have received little attention. Only a few hydroxy acids containing aromatic rings have been briefly examined.

Tishchenko et al. (60) extracted lanthanide salts of mandelic acid into butanol. D increased with z up to samarium, after which the lanthanides were initially solubilized into the organic phase only to later separate as flocculant precipitates. Using the method of isomolar series with Nd, the extracting species was determined to be $NdA_3(HA)$. Benzilic acid was used by Mishchenko et al. (61) with Rhodamine S to effect lanthanide extraction into benzene. The extracting species is probably ion-paired. The dihydroxy acid, 2,3-dihydroxy naphthoic acid was employed (62) to extract lanthanides into a variety of polar solvents. In the presence of 1,10-phenanthroline, a mixed species was extracted into either benzene or $CHCl_3$. The species was determined by both the isomolar series and molar ratio methods to be LnA_3(phen).

IV. EXPERIMENTAL

A. 2,5-Dimethyl-2-hydroxyhexanoic Acid

The 2,5-dimethyl-2-hydroxyhexanoic acid (DMHHA) was first prepared by Dr. J. E. Powell and Mr. H. R. Burkholder _via_ the following reaction scheme:



About 300 g of crude product (45% yield) were kindly provided by the above and were recrystallized from a 1:1 mixture of toluene and Skelly C. This recrystallized acid melted between 82-83°C. The formula weight was potentiometrically determined to be 161 (theoretical: 160). Elemental analysis gave 59.9% carbon and 10.2% hydrogen (theoretical: 60.0% carbon and 10.0% hydrogen). DMHHA was found to be very soluble in chloroform and hexanol, and moderately soluble in ether, toluene, water and Skelly C.

B. Reagents

1. Lanthanide nitrate solutions

Solutions of approximately 0.1 M $Ln(NO_3)_3$ were made by dilution of concentrated stock solutions. These concentrated solutions had been previously prepared from the corresponding lanthanide oxides (greater than 99.9% purity) by Mr. James Farrell, using the method described by Adolphson (63). The dilute lanthanide nitrate solutions were standardized gravimetrically by precipitating the metal as the oxalate and ashing to the oxide. Some of the solutions were standardized by complexometric titration with EDTA, using xylenol orange as an indicator.

2. Potassium hydroxide solution

The standard potassium hydroxide solution was prepared by diluting ampoules of carbonate-free KOH (Anachemia) with boiled deionized water. This was kept in a large carboy and protected by an Ascarite/Drierite trap. The base was standardized by numerous titrations of primary standard grade potassium acid phthalate.

3. Potassium nitrate solution

An approximately 0.1 M solution of potassium nitrate was prepared by dissolving reagent grade KNO_3 in boiled deionized water. It was standardized by loading aliquots of the KNO_3 solution onto hydrogen-form Dowex 50W-X8 resin, thoroughly rinsing, and titrating the resultant eluant acid with standard KOH.

4. Nitric acid solution

The nitric acid solutions were made from reagent grade HNO_3 and were standardized by titrations with standard KOH.

5. DMHHA solutions

Solutions of DMHHA in chloroform, hexanol, and water were all standardized by titration against standard base. In preparing solutions of completely neutralized DMHHA, a known amount of KOH was added to a weighed amount of acid and the volume brought to 100 milliliters. Five milliliter aliquots of this resultant solution were titrated with base to check the amount of remaining unneutralized acid. A seventy-five milliliter portion was then removed, completely neutralized, and diluted to 200 milliliters.

6. ^{147}Neodymium nitrate solution

The ^{147}Nd was made at the Ames Laboratory Research Reactor by neutron bombardment of either high purity Nd_2O_3 or an evaporated sample of high purity $Nd(NO_3)_3$. The specific activity produced was approximately 500 millicuries per gram. After deencapsulation and one day of cooling, the radioactive neodymium was dissolved in 5 ml of 0.1 M HNO_3 and diluted to the desired volume.

7. ^{170}Thulium nitrate solution

^{170}Thulium chloride was purchased from New England Nuclear and had a specific activity on receipt of about 40 millicuries per milligram. It was isotopically diluted by a factor of 50 with 169-thulium nitrate.

C. Acid Anion Protonation Constant

The acid anion protonation constant was obtained from pH_c measurements on a series of independently prepared DMHHA solutions, each containing a different amount of added KOH. Prior to measurement, the solutions were equilibrated in a water bath thermostatted to 25.00 ± .05°C for 12-24 hours. The ionic strength of each solution was adjusted by the addition of an appropriate amount of KNO_3. This KNO_3 amount was calculated from an estimated protonation constant using the iterative computer program ALFA (see Appendix).

The pH_c measurements were made in a closed thermostatted vessel under a nitrogen atmosphere. A Corning Model 101 Digital Electrometer equipped with a Beckman glass electrode, a Beckman sleeve-type reference electrode and a platinum ground wire, was used in making the measurements. The instrument was calibrated and sloped with a series of concentration standards. These were nonbuffered HNO_3 solutions adjusted to 0.1 $\underline{M}$ ionic strength. As a consequence, the hydrogen ion concentration rather than activity were read from the meter. In making the pH_c readings, the electrodes are first rinsed with the solution to be measured, and then successive portions of the solution are read until stability is obtained.

D. Lanthanide-DMHHA Stability Constants

Solutions containing fixed amounts of metal and variable amounts of DMHHA and KOH were adjusted to 0.1 M ionic strength with KNO_3. The amount of KNO_3 which was added was calculated from the estimated stability constants $\beta_x = [MA_x]/[M][A]^x$ using the program BETA (see Appendix). The pH_c measurements were made in the manner previously mentioned. The stability constants were calculated using a multiple linear regression scheme incorporated into the program OMEGA (see Appendix). The equations involved in these calculations are discussed in a later chapter.

E. Acid Distribution Experiments

The DMHHA chloroform-water partition constant and the DMHHA dimerization constant (in $CHCl_3$) were obtained from experiments on the distribution of the acid between the two solvents. Typically, a known amount of acid in chloroform was placed in a centrifuge tube containing 6 ml of an aqueous phase (0.1 M ionic strength) and a volume of chloroform needed to bring the organic phase volume to 6 ml. The sample was thoroughly shaken for about one minute and then placed in a temperature bath and allowed to equilibrate for about 48 hours. After equilibration, the sample was centrifuged and any volume changes noted. Aliquots from each phase were then removed and the acid concentrations determined by titration with standard base. Optimum results for the chloroform phase were obtained by allowing the chloroform to evaporate before titrating the DMHHA.

F. Osmometric Measurements

Osmometry was used to provide additional information on the acid distribution behavior. A Mechrolab 301A Osmometer equipped with two 25°C nonaqueous thermistor probes was graciously provided by Dr. R. J. Angelici and Dr. J. G. Verkade for use in these studies. The instrument was calibrated with solutions of benzil in water-saturated chloroform.

G. Macroscopic Distribution Experiments

In the distribution experiments of macroscopic amounts of Ln^{3+} between two solvents, various amounts of metal DMHHA and base were combined in a separatory funnel together with enough KNO_3 to bring the aqueous phase ionic strength to 0.1 M. The initial volumes of both solvents were the same, usually 100 milliliters. The separatory funnel was well-shaken and equilibrated for a period of a few days. The pH of the aqueous phase was then measured and the two phases separated. The metal in the aqueous phase was determined by complexometric titration with EDTA.

The amount of metal in the organic phase was obtained by one of two different methods. In one method, the metal was re-extracted into 3 M HCl and then titrated with EDTA. The other method involved a two-phase precipitation with oxalic acid, followed by slow filtration of the metal oxalate and subsequent ashing to the oxide. Both methods gave reasonably good analyses, but neither was well-suited for small samples.

In some of the distribution experiments, the acid content of the aqueous phase was needed. This was obtained directly by titration with standard base in the presence of a small amount of copper.

H. Microscopic Distribution Experiments

Fifteen-milliliter glass-stoppered centrifuge tubes were employed in the distribution experiments of tracer level lanthanides. The aqueous and chloroform phases were prepared prior to adding the tracer metal with either an Eppendorf pipet or Finnpipet. The centrifuge tubes were thoroughly shaken and equilibrated in a thermostatted bath (25.00 ± .05°C) for several days, after which they were centrifuged.

The aqueous pH and the phase volumes were noted and portions of each phase removed for metal determination. To avoid contamination of the lower phase, a positive pressure must be maintained through the upper phase when sampling from the lower phase.

For neodymium, the aliquots (usually 2-4 ml) were placed in polyethylene vials suitable for gamma counting. The metal content of each phase was determined with a well-type thallium doped NaI scintillation counter kindly made available by Dr. A. F. Voigt and Mr. W. A. Stenoland. The entire γ-spectrum from 0.091 MeV to 0.688 MeV was usually used in counting. To achieve good statistical analyses, greater than 40,000 counts were usually obtained. The background counting rate was noted and subtracted from the total counting rate.

The thulium tracer was counted using a Beckman liquid scintillation system graciously provided by the Health Physics Group of the Ames Laboratory. High quality polyethylene scintillation vials and a dioxane based scintillation cocktail were used.

I. Separation Factors

The separation factors were either obtained directly from lanthanide determinations, or indirectly from the ratio of the distribution ratios, $\alpha_{Ln_1}^{Ln_2} = \frac{D(Ln_2)}{D(Ln_1)}$. In the direct determinations, two lanthanides were simultaneously extracted and the amount of each determined by flame emission photometry. The flame emission analyses were performed by an analytical group of the Ames Laboratory and were, unfortunately, frequently unsatisfactory. Only on those occasions where the emission analyses agreed with the titration analyses and with the individual lanthanide mass balances were the separation factors calculated.

V. PRELIMINARY EXTRACTIONS AND ACID STUDIES

A. Preliminary Extractions

As has been mentioned in an earlier chapter, no aliphatic hydroxy carboxylic acids have yet been studied as extracting agents for the lanthanides. 2,5-Dimethyl-2-hydroxyhexanoic acid (DMHHA) was chosen as the subject for the present work, primarily due to its favorable carbon number (8) and the availability of the precursor ketone.

Prior to an extensive investigation of the acid, preliminary lanthanide extraction studies were performed to see if further investigations would even be profitable. No extraction into toluene was observed, but extractions using chloroform as a diluent produced some interesting results (Table 1). Substantial extraction of both praseodymium and

Table 1. Preliminary lanthanide extractions

Ln^{3+}	A^-/Ln^{3+}	HA_f^a/Ln^{3+}	Base	% Extn.	% Precip.
Pr	3	1	KOH	65	0
Pr	3	1	Bu_4NOH	65	0
Nd	4	1	KOH	76	8
Nd	4	1	Bu_4NOH	90	0
Er	4	1	KOH	0	81
Er	4	1	Bu_4NOH	26	70

[a] HA_f represents total unneutralized acid.

neodymium were seen. The heavy lanthanide erbium, was not extracted except in the presence of the organic-soluble tetrabutyl ammonium cation. This cation also enhanced the extraction of neodymium, but had no apparent effect on the praseodymium partition. Because of this interesting lanthanide extraction behavior, chloroform was chosen as the solvent to be used in further investigations. Before proceeding with additional lanthanide extractions, more information was needed on DMHHA's behavior in the two solvents.

B. Acid Anion Protonation Constant

The acid anion protonation constant ($\alpha = [HA]/[H^+][A^-]$) of DMHHA was obtained from pH measurements on solutions of partially neutralized acid. The mass balance equations involved are:

$$\text{Total Acid} = H_T = [HA]_{init} - [KOH] = [H^+] + [HA]$$

$$\text{Total Anion} = A_T = [A^-] + [HA]$$

Substituting for [HA] and taking the ratio of the two equations yields

$$\frac{H_T - [H^+]}{A_T} = \frac{\alpha[H^+]}{1 + \alpha[H^+]}$$

This can be rearranged to give $\alpha = ([H^+] - H_T)/(H_T - [H^+] - A_T)[H^+]$ from which the protonation constant can be directly computed. The value of α which was thusly obtained is 6.09×10^3.

C. Acid Distribution Studies

The distribution behavior of DMHHA between chloroform and water is depicted in Figure 1, where E is defined as the ratio of the concentrations of total unionized organic acid to total unionized aqueous acid. As can be seen, E varies linearly with $[HA]_a$ in the concentration range shown. This can be explained by considering the following equilibria:

$$P_{HA} = [HA]_o/[HA]_a \qquad K_{D,O} = [H_2A_2]_o/[HA]_o^2 \ .$$

If the DMHHA is present in the organic phase as a mixture of monomers and dimers, a linear relationship between E and $[HA]_a$ would be obtained:

$$E = \frac{\Sigma(HA)_o}{\Sigma(HA)_a} = \frac{[HA]_o + 2[H_2A_2]_o}{[HA]_a} = P_{HA} + 2K_{D,O}(P_{HA})^2[HA]_a \ .$$

The values of P_{HA} and $K_{D,O}$ derived from the graph are 1.0 and 56, respectively. At higher concentrations of $(HA)_a$ (exceeding those used in the lanthanide extraction experiments), E shows a pronounced upward swing.

The relationship of the acid distribution to the ionic strength of the aqueous phase was determined and is shown in Figure 2. A definite salting-out effect was observed.

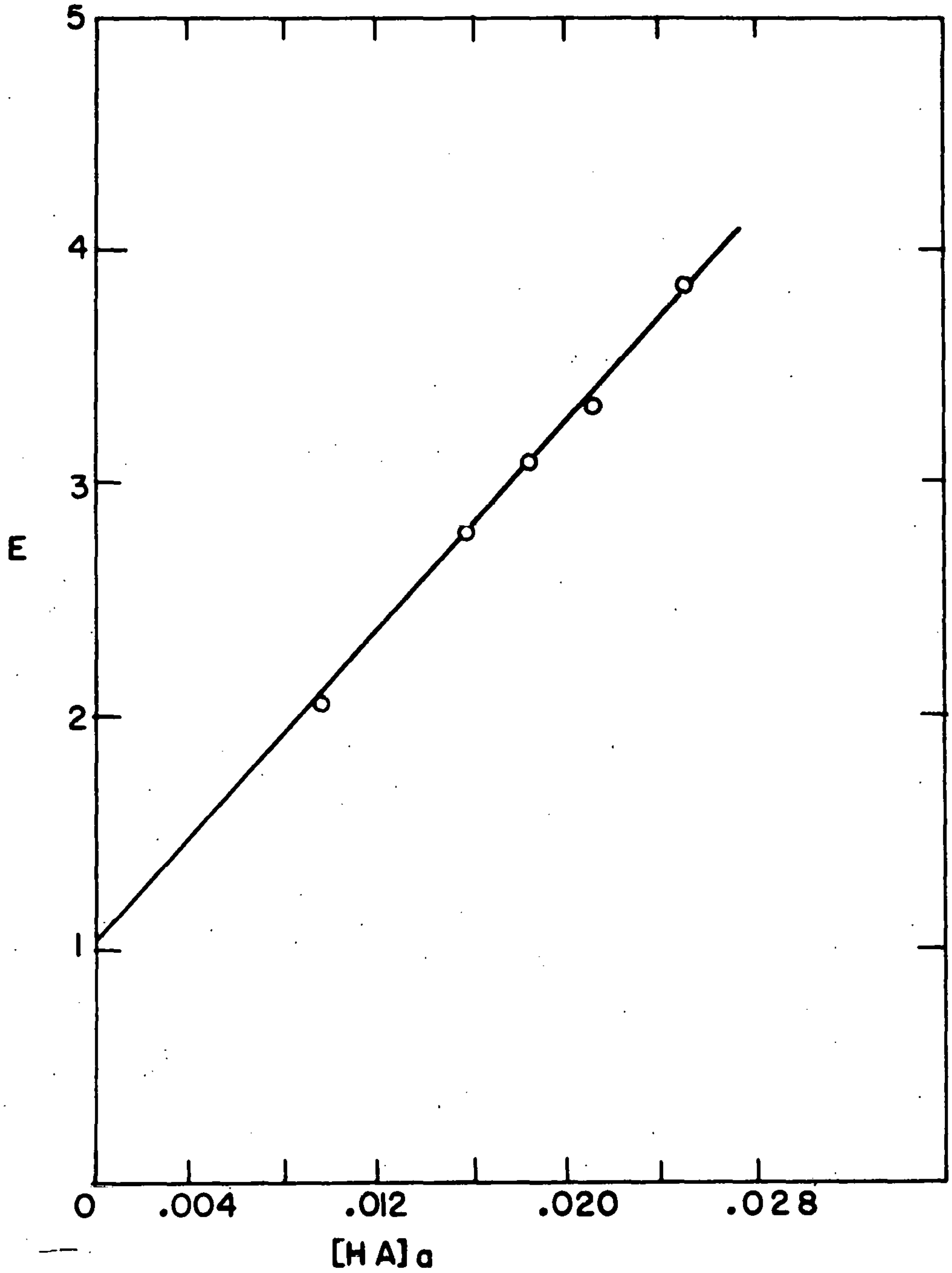


Figure 1. DMHHA distribution between chloroform and water as a function of aqueous acid concentration

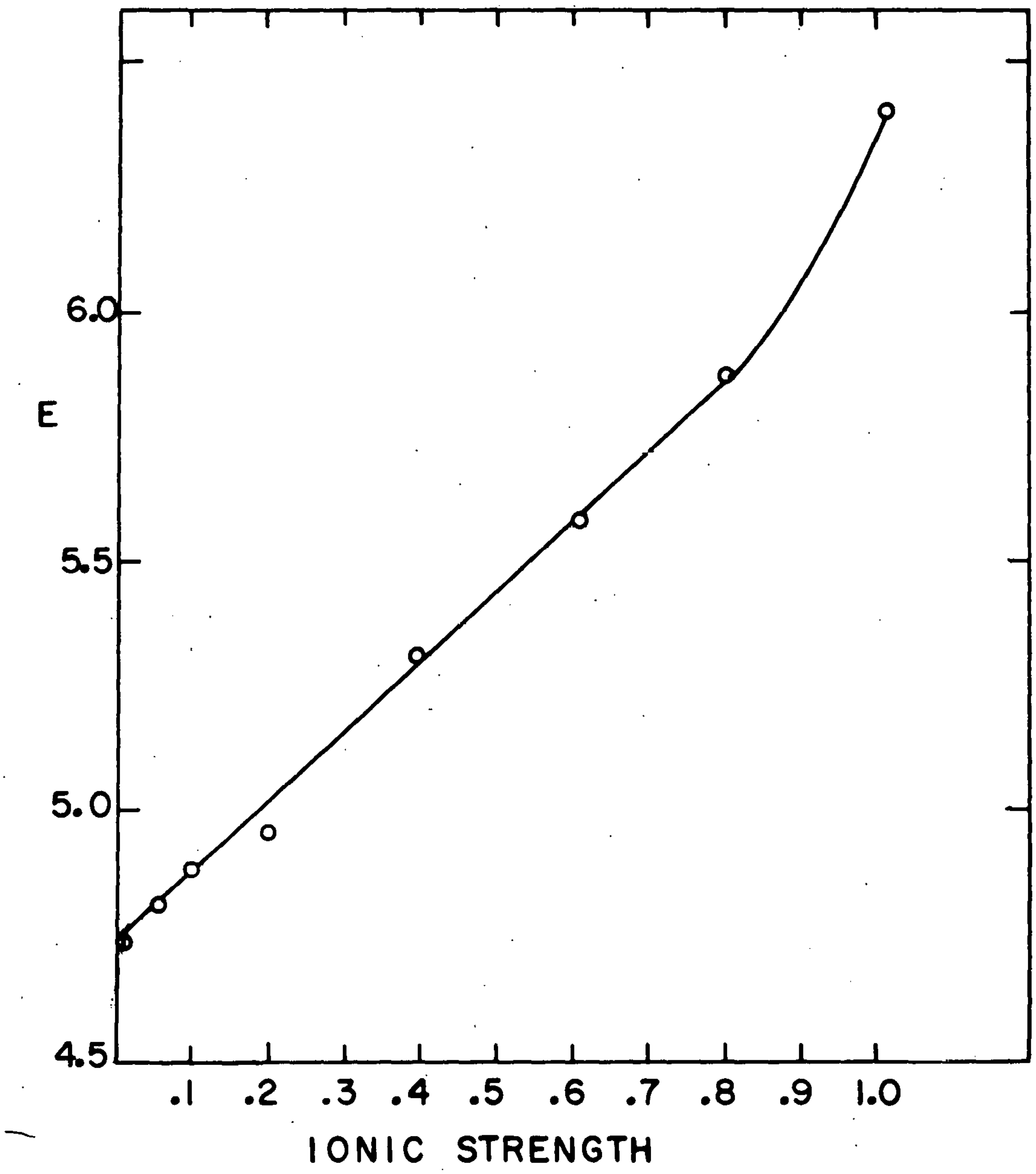


Figure 2. DMHHA distribution between chloroform and water as a function of ionic strength

D. Infrared Spectroscopy

A confirmation of the above monomer-dimer explanation of the DMHHA distribution behavior was desired. Infrared spectroscopy has been used (64-66) with a variety of carboxylic acids to study the monomer-dimer equilibrium. The carboxylic acid monomer generally exhibits a sharp OH band around 3500 cm^{-1} and a C=O stretch around 1770 cm^{-1}. For the dimeric species a broad irregular band between 3500 and 2300 cm^{-1}, and a C=O band at 1720 cm^{-1} are usually observed.

The typical infrared spectrum of DMHHA displayed a sharp band at 2960 cm^{-1} on top of a broad but not intense band ranging from 3200 to 2800 cm^{-1}. The C=O band was observed at 1720 cm^{-1}. At low acid concentrations, a very weak band may be appearing at 1770 cm^{-1}. The monomer band expected at 3500 cm^{-1} was apparently not present. No significant changes in the spectrum occurred with changes in the DMHHA concentration.

This infrared behavior of DMHHA does not lend itself to easy analysis. The most logical explanation for its divergent behavior lies in the fact that it is an α-hydroxy carboxylic acid. The presence of the α-hydroxy group permits intramolecular hydrogen bonding not present in the acids previously studied. Such bonding could significantly alter the infrared spectrum.

E. Osmometry

Osmometry has been frequently used to determine the molecular association of species present in solution. It was thought that it could provide some further insight into the nature of DMHHA in chloroform.

In a thermoelectric osmometer, a sample of solvent and a sample of solution are introduced onto two thermistor probes contained in a thermostatted system in equilibrium with solvent vapor. Since the vapor pressure of the solution is lower than that of the solvent, solvent vapor condenses onto the solution sample, causing its temperature to rise. For an ideal solution, this increase is given by $\Delta T = RT^2m/\Delta H_v \cdot 1000$, where ΔH_v is the heat of vaporization of the solvent and m is the molality of the solution. In practice, small heat losses can occur, and the instrument is usually calibrated using standard solutions of a solute which is strictly monomeric in solution.

In these experiments, the instrument was calibrated with benzil to read molarity instead of molality. The calibration curve is shown in Figure 3. From five DMHHA water-chloroform distribution solutions, constants of $K_{D,O} = 56$ and $P_{HA} = 1.0$ were obtained. Aliquots of the organic phase from each solution were then measured osmometrically. From these measurements and titration measurements of the total acid in the organic phase, the

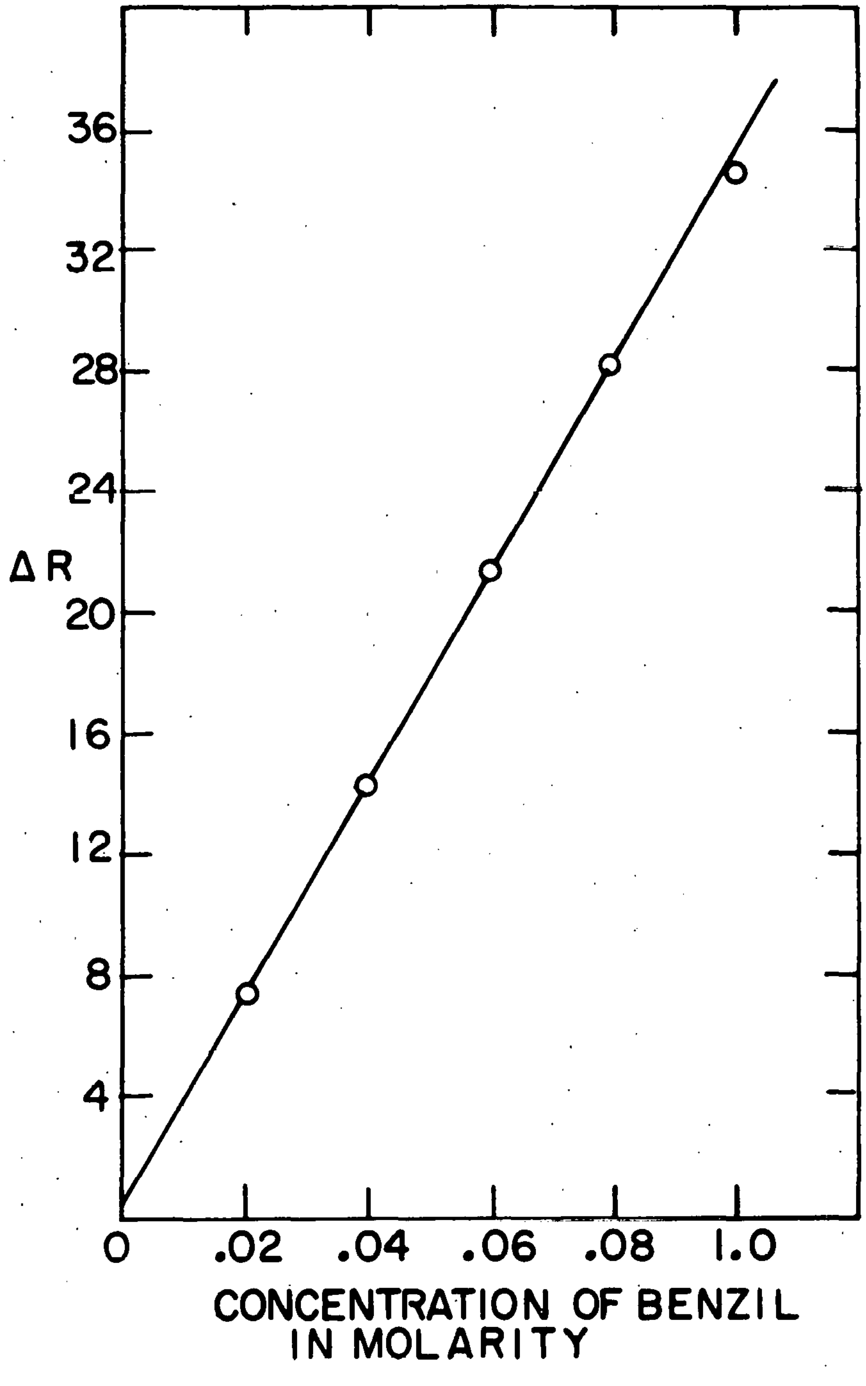


Figure 3. Calibration curve used in osmometric measurements

amounts of acid monomer and dimer were calculated:

$$\text{Total Acid} = [HA] + 2[H_2A_2]$$

$$\text{Total Molar Species} = [HA] + [H_2A_2]$$

The acid dimerization constant was then computed and found to equal 56 ± 4. This is in excellent agreement with the value of $K_{D,O}$ obtained otherwise, and confirms the monomer-dimer explanation of the distribution behavior.

VI. RESULTS AND DISCUSSION

A. Neodymium-DMHHA Stability Constants

The main point of interest in most metal extraction studies is the means by which the metal extracts, that is, the nature of the extracting species. Once the behavior of the extractant is defined, one more study should be performed before proceeding to this topic. The aqueous phase interaction between the metal and the extracting agent should be investigated. This usually involves measuring the stability constants $\beta_x = [MA_x]/[M][A]^x$.

Rather than studying all of the lanthanides, one was chosen for detailed analysis in this investigation. Neodymium was selected because of its purplish color (which makes extractions easy to follow), and because of the availability of the neodymium-147 tracer (in case tracer work would be desired).

The experimental method used for obtaining the stability constant data was explained earlier. The stability constant calculations will now be discussed.

The pertinent mass balance equations for the total acid anion concentration and the total metal concentration are:

$$[A]_{tot} = [A] + [HA] + [MA] + 2[MA_2] + 3[MA_3] + \ldots + x[MA_x]$$

$$[A]_{tot} = [A] + \alpha[H][A] + \beta_1[M][A] + 2\beta_2[M][A]^2 + \ldots + x\beta_x[M][A]^x \qquad (8)$$

$$[M]_{tot} = [M] + [MA] + [MA_2] + [MA_3] + \ldots + [MA_x]$$

$$[M]_{tot} = [M] + \beta_1[M][A] + \beta_2[M][A] + \ldots + \beta_x[M][A]^x \qquad (9)$$

where for convenience the charges on the ions are omitted. Rearranging and dividing equation (8) by equation (9) yields:

$$\frac{[A]_{tot} - [A] - \alpha[H][A]}{[M]_{tot}} = \frac{\sum_{1}^{x} x \; \beta_x[A]^x}{1 + \sum_{1}^{x} \beta_x[A]^x}$$

With cross multiplication and further rearrangement, an equation amenable to multiple linear regression emerges:

$$[A] + \alpha[H][A] - [A]_{tot} = \sum_{1}^{x} ([A]_{tot} - [A] - \alpha[H][A] - x[M]_{tot})\beta_x[A]^x$$

$$Y = X_1\beta_1 + X_2\beta_2 + X_3\beta_3 + \ldots + X_x\beta_x$$

All of the quantities except the β's are known or directly measurable. The value of [A] is obtained <u>via</u> a pH measurement and the equation $[A] = ([H]_{tot} - [H])/\alpha[H]$. Measuring the pH value under <u>i</u> different conditions gives <u>i</u> equations.

$$Y_i = X_{1i}\beta_1 + X_{2i}\beta_2 + X_{3i}\beta_3 + \ldots + X_{xi}\beta_x$$

(At this point for further simplification, the value of <u>x</u> is made equal to 3). This system of i equations and 3 unknowns is solved by a least-squares multiple linear regression.

The least-squares analysis proceeds by minimizing the sum of the squares of the individual residuals ε_i. The residual is defined as the difference between the observed Y_i and the Y_i predicted using the calculated β's. The

$$\varepsilon_i = Y_i - X_{1i}\beta_1 + X_{2i}\beta_2 + X_{3i}\beta_3$$

sum of the squares is minimized by taking the individual first derivatives and setting them equal to zero.

$$S = \sum_i \varepsilon_i^2 = \sum_i (Y_i - \beta_1 X_{1i} - \beta_2 X_{2i} - \beta_3 X_{3i})^2$$

$$\frac{\partial S}{\partial \beta_1} = -2 \sum_i X_{1i}(Y_i - \beta_1 X_{1i} - \beta_2 X_{2i} - \beta_3 X_{3i}) = 0$$

$$\frac{\partial S}{\partial \beta_2} = -2 \sum_i X_{2i}(Y_i - \beta_1 X_{1i} - \beta_2 X_{2i} - \beta_3 X_{3i}) = 0$$

$$\frac{\partial S}{\partial \beta_3} = -2 \sum_i X_{3i}(Y_i - \beta_1 X_{1i} - \beta_2 X_{2i} - \beta_3 X_{3i}) = 0$$

Rearranging, this yields the following equations:

$$\Sigma\, \beta_1 X_{1i}^2 + \Sigma\, \beta_2 X_{1i} X_{2i} + \Sigma\, \beta_3 X_{1i} X_{3i} = \Sigma\, X_{1i} Y_i$$

$$\Sigma\, \beta_1 X_{1i} X_{2i} + \Sigma\, \beta_2 X_{2i}^2 + \Sigma\, \beta_3 X_{2i} X_{3i} = \Sigma\, X_{2i} Y_i$$

$$\Sigma\, \beta_1 X_{1i} X_{3i} + \Sigma\, \beta_2 X_{2i} X_{3i} + \Sigma\, \beta_3 X_{3i}^2 = \Sigma\, X_{3i} Y_i$$

One now has a system of 3 equations and 3 unknowns which can be represented in matrix form and readily solved.

$$\begin{bmatrix} \Sigma X_{1i}^2 & \Sigma X_{1i}X_{2i} & \Sigma X_{1i}X_{3i} \\ \Sigma X_{1i}X_{2i} & \Sigma X_{2i}^2 & \Sigma X_{2i}X_{3i} \\ \Sigma X_{1i}X_{3i} & \Sigma X_{2i}X_{3i} & \Sigma X_{3i}^2 \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \end{bmatrix} = \begin{bmatrix} \Sigma X_{1i}Y_i \\ \Sigma X_{2i}Y_i \\ \Sigma X_{3i}Y_i \end{bmatrix} \qquad (10)$$

The above multiple linear regression, as described by Draper and Smith (67), was incorporated into the computer program OMEGA, a modified form of a program written by D. A. Johnson (68). The solution to equation 10 is obtained using DGELG, a doubly pivoted Gaussian elimination routine, available on the IBM 360 computer (69).

Because some points inherently contain greater relative errors than others, the regression is weighted. The individual weighting factors w_i are obtained from the standard errors, q_i, $w_i = \frac{1}{q_i^2}$. These, in turn, are derived from the individual residuals, ε_i. By the law of propagation of errors $q_i = (\frac{\partial \varepsilon_i}{\partial A_T})q'_{A_T} + (\frac{\partial \varepsilon_i}{\partial [A]})q'_{[A]} + (\frac{\partial \varepsilon_i}{\partial M_T})q'_{M_T}$ where $q'_c = (\frac{\sigma_c}{c}) \cdot c$. σ_c is the standard deviation of c and the quotient $(\frac{\sigma_c}{c})$ is the average relative error in c. The average relative errors used in the present computations were generally around .005. Since the values of the β's need to be known to calculate the weighting factors, an iterative procedure was used.

The neodymium-DMHHA stability constants which were obtained in the above manner are listed below.

$$\beta_1 \times 10^{-2} = 4.71\ (.08)$$

$$\beta_2 \times 10^{-4} = 4.27\ (.33)$$

$$\beta_3 \times 10^{-6} = 1.64\ (.34)$$

The standard deviations are given in partheneses and were obtained from $\sigma_{\beta_n} = \pm \sqrt{c_{ii}\ S^2}$, where c_{ii} is the i^{th} diagonal element of the inverse coefficient matrix and S^2 is the estimate of the variance in the regression (67).

B. Macroscopic Neodymium Extractions

In the majority of lanthanide extraction studies where the extracting species has been determined, the pertinent information was obtained using tracer level lanthanides. Unfortunately, the chemistry of tracer level extractions and macroscopic level extractions occasionally differs. Since most practical extraction applications involve macroscopic quantities of lanthanides, the present work was initially focused on macro-scale extractions.

In a series of neodymium extraction experiments, measurements were made of the total metal concentration in both phases, and of the total acid and hydrogen ion concentrations in the aqueous phase. These measurements, in conjunction with a few assumptions and the previously obtained constants ($K_{D,O}$, P_{HA}, K_A, β_1, β_2, β_3), should reveal the extracted species. If it is assumed that no A^- was present in the organic phase and that no cationic species, *e.g.*, $MA_2^+NO_3^-$, were extracted, then the extracted species may be represented as $MA_x(HA)_n$, where *x* and *n* may be determined from mass balance considerations.

Using $[H]_{tot,a} - [H^+] = [HA]_a$ to first obtain $[HA]_a$, the equation for the acid anion protonation constant was then used to calculate the $[A^-]_a$. The aqueous amounts of M^{3+}, MA^{2+}, MA_2^+, and MA_3 were determined from the expression for $[M]_{tot,a}$

$$[M]_{tot,a} = [M] + [MA] + [MA_2] + [MA_3]$$
$$= [M] \cdot \left(\sum_{x=0}^{3} \beta_x [A]^x \right) .$$

From consideration of the acid anion mass balance, the total amount of anion in the organic phase, $[A]_{t,o}$, was obtained.

$$[A]_{tot,o} = (A_T - ([A]_a - [HA]_a - [MA]_a - 2[MA_2]_a - 3[MA_3]_a)V_a)/V_o$$

V_a and V_o represent the aqueous and organic volumes, respectively. The total amount of acid in the organic phase, $[H]_{tot,o}$, was similarly determined from the total acid mass balance.

The amount of anion bound to the extracted metal, $[A]_{b,o}$, was calculated by subtracting $[H]_{tot,o}$ from $[A]_{tot,o}$. The value of $\underline{x}$ finally obtained from the expression $[A]_{b,o}/[M]_{tot,o} = \underline{x}$, was 3.0 ± 0.1. This value of $\underline{x}$ is what one would expect for the extraction of a trivalent metal.

The determination of n proceeded in a similar fashion. The concentrations of $(HA)_o$ and $(H_2A_2)_o$ were obtained from $[HA]_a$, P_{HA} and $K_{D,O}$ and subtracted from $[H]_{tot,o}$ to give the total amount of bound acid $[HA]_{b,o}$. Calculation of $\underline{n}$ from $[HA]_{b,o}/[M]_{tot,o}$ produced numbers ranging from near zero to almost four. Apparently, the extraction of the metal had an effect on the acid partition and/or dimerization. This would change the value of P_{HA} and/or $K_{D,O}$ which would invalidate the above approach for finding $\underline{n}$.

In an attempt to eliminate the effect of the metal partition on the acid behavior, some experiments were performed at very high $[HA]_o$ to metal ratios. Unfortunately, under such conditions the metal extraction was limited as extensive precipitation occurred. Thus, in order to achieve metal extraction at the high acid to metal ratios needed to determine $\underline{n}$, tracer scale work was needed.

Prior to the tracer experiments, further macroscopic neodymium extractions produced some interesting results (Table 2). As can be seen, an increase in the metal concentration produced a substantial increase in the

Table 2. Macroscopic neodymium extractions

Sample	Nd_i^{3+}[a]	A^-/Nd^{3+}	HA_f/Nd^{3+}	D	% Extn.
A	.00531	4	4.6	11	91
B	.0106	4	5.3	35	97
C	.0213	4	5.4	136	99
D	.00531	4	4.6	11	91
E	.00531	4	14.5	13	93
F	.00531	4	33.2	21	95
G	.00531	4	0.33	7.1	65
H	.00531	4	0.15	7.0	68
I	.0021	3.5	1.0	0.83	44
J	.0064	3.5	0.33	1.35	14[b]
K	.0106	3.5	0.2	2.83	14[b]
L	.0213	3.5	0.05	5.1	9[b]

[a] Initial concentration of neodymium in aqueous phase.

[b] Accompanied by significant precipitation.

distribution coefficient. An increase in the free acid concentration produced a similar, though lesser, effect. In experiments G and H, significant extraction was observed, despite a free acid-to-metal ratio of less than one. In contrast, J-L produced little extraction, but extensive precipitation. When enough additional free acid was added to these samples to bring the ratio to around one, the precipitate redissolved and significant extraction was observed.

C. Tracer-Level Neodymium Extractions

In a series of tracer extractions holding $[HA]_o$ constant, the values of both D and $[H^+]$ were measured. Using the equation, $(M^{x+})_a + (x + n)(HA)_o \rightleftarrows (MA_x(HA)_n)_o + X(H^+)_a$, to represent the metal extraction, the equation, $\log D = \log K + (n + x) \log [HA]_o - x \log [H^+] - \log (\Sigma\ \beta_x[A]_a^x)$, was obtained as described earlier. The value of <u>x</u> was then secured from the slopes of $\log D + \log (\Sigma\ \beta_x[A]_a^x)$ *versus* pH plots. (A typical plot is shown in Figure 4.) As expected, the individual slopes obtained were around three, the number calculated from the macroscopic experiments. Unfortunately, and rather surprisingly, the slopes varied from a low of about 3 to a high of approximately 3.7.

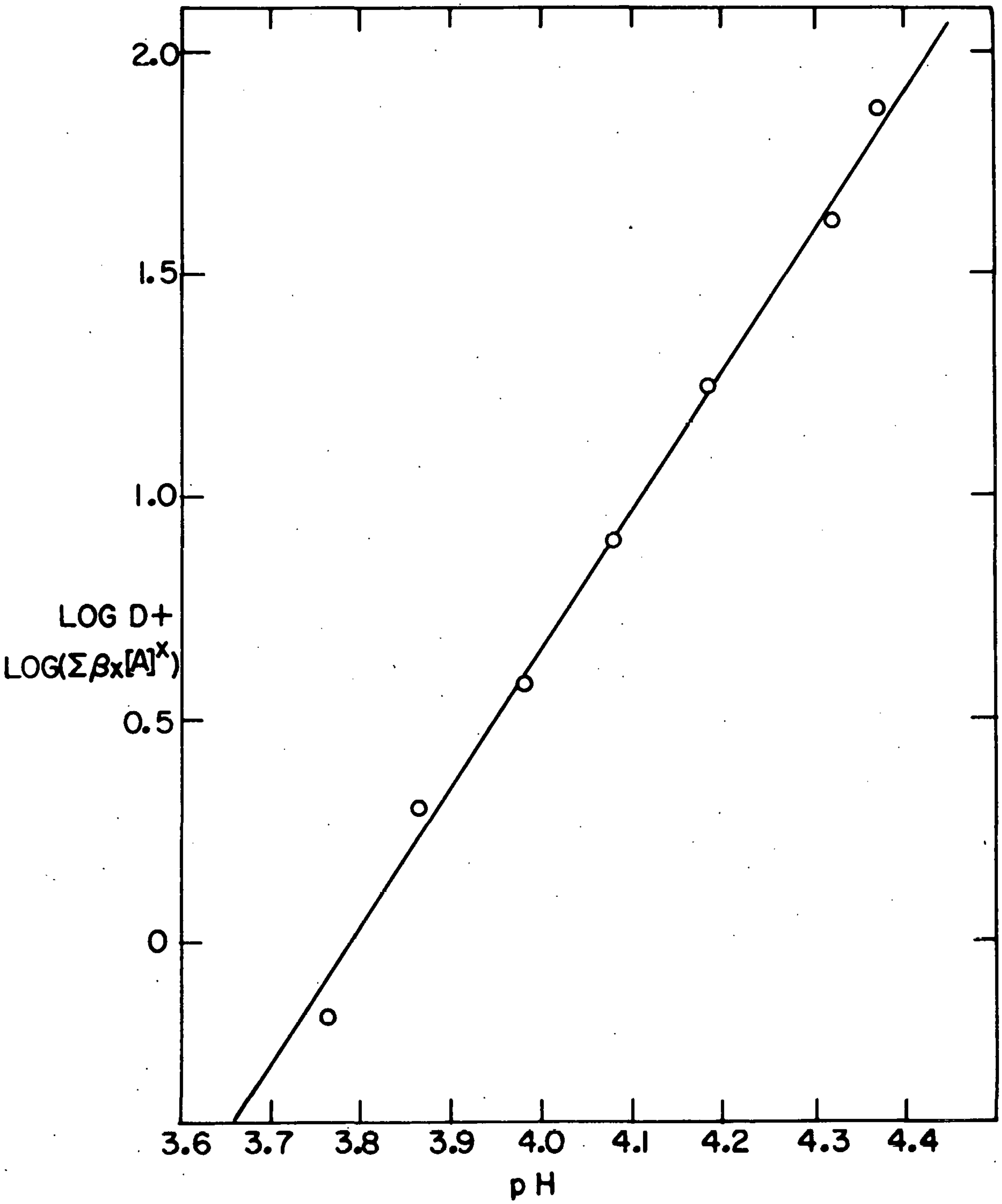


Figure 4. pH dependency of log D + log ($\Sigma\ \beta_x[A]^x$)

The value of n was acquired in a similar fashion. In a series of experiments holding the pH constant, the distribution ratios were measured. In each sample, in order to obtain the desired pH prior to its actual measurement, the hydrogen ion concentration was estimated from equilibria considerations. To accomplish this, the system of five unknowns ($(HA)_a$, $(H^+)_a$, $(A^-)_a$, $(HA)_o$, $(H_2A_2)_o$) and five equations (total acid, total acid anion, $K_{D,O}$, P_{HA}, α) was solved iteratively in the computer program EXTN (see Appendix). Later, to decrease the total computation time, the iteration was programmed onto a magnetic card for use in a Texas Instruments SR-52 calculator (see Appendix). The concentrations of $(A^-)_a$ and $(HA)_o$ were also obtained from this program. Using these concentrations, plots of $\log D + \log (\Sigma\ \beta_x[A]_a^x)$ versus $[HA]_o$ were made to procure n.

A slightly altered approach was also used for obtaining the value of n. Representing the extraction equilibrium (perhaps more realistically) as $(M^{x+})_a + x(A^-)_a + n(HA)_o \rightleftarrows (MA_x(HA)_n)_o$, the accompanying log equation becomes $\log D = \log K' + n \log [HA]_o + x \log [A^-]_a - \log (\Sigma\ \beta_x[A^-]_a^x)$. Using this approach, experiments were done holding $[A^-]$ constant, varying $[HA]_o$ and measuring the resultant distribution ratios. As in the previous experiments n was obtained from the slopes of the log-log plots. (A typical plot is shown in Figure 5.) This approach as well as the other approach both yielded a value of n of 5.0 ± 0.3.

Though the results for the determination of n were satisfactory, the variable answers obtained for x were the cause of some concern. It was thought that perhaps more than one species was extracting, specifically, that the extracting monomer might be dimerizing.

If a monomer and dimer were both extracting, the distribution ratio would be represented as:

$$D = \frac{[MA_x(HA)_n]_o + [(MA_x)_2(HA)_m]_o}{[M^{x+}]_a \cdot (\sum_x \beta_x [A^-]^x)}$$

$$D = K[A^-]^x[HA]_o^n/(\sum_x \beta_x[A^-]^x) + (K'[A]^{2x}[HA]_o^m/(\sum_x \beta_x[A^-]^x))[M^{x+}]_a$$

At constant $[A^-]_a$ and $[HA]_o$, the above equation would simplify to a linear equation in $[M^{x+}]_a$. To evaluate this possibility, a series of extractions was performed in which $[A^-]_a$ and $[HA]_o$ were both held constant and D was measured as a function of $[M^{x+}]_a$. The data which resulted are graphed in Figure 6. A definite linear trend was observed, suggesting the extraction of both a monomeric and a dimeric species.

The extraction of more than one species placed in doubt the previously obtained value of n, since the

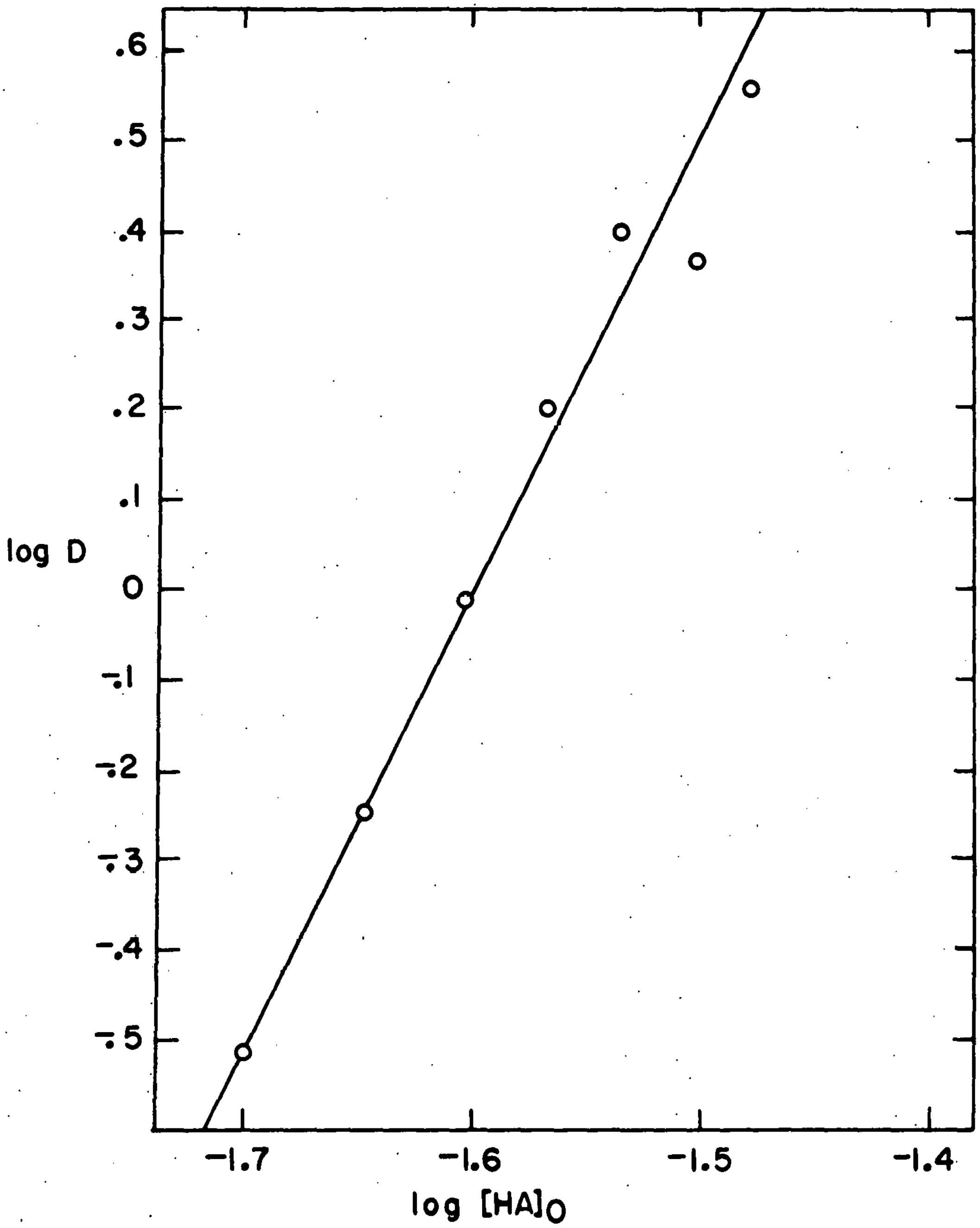


Figure 5. D as a function of log $[HA]_o$

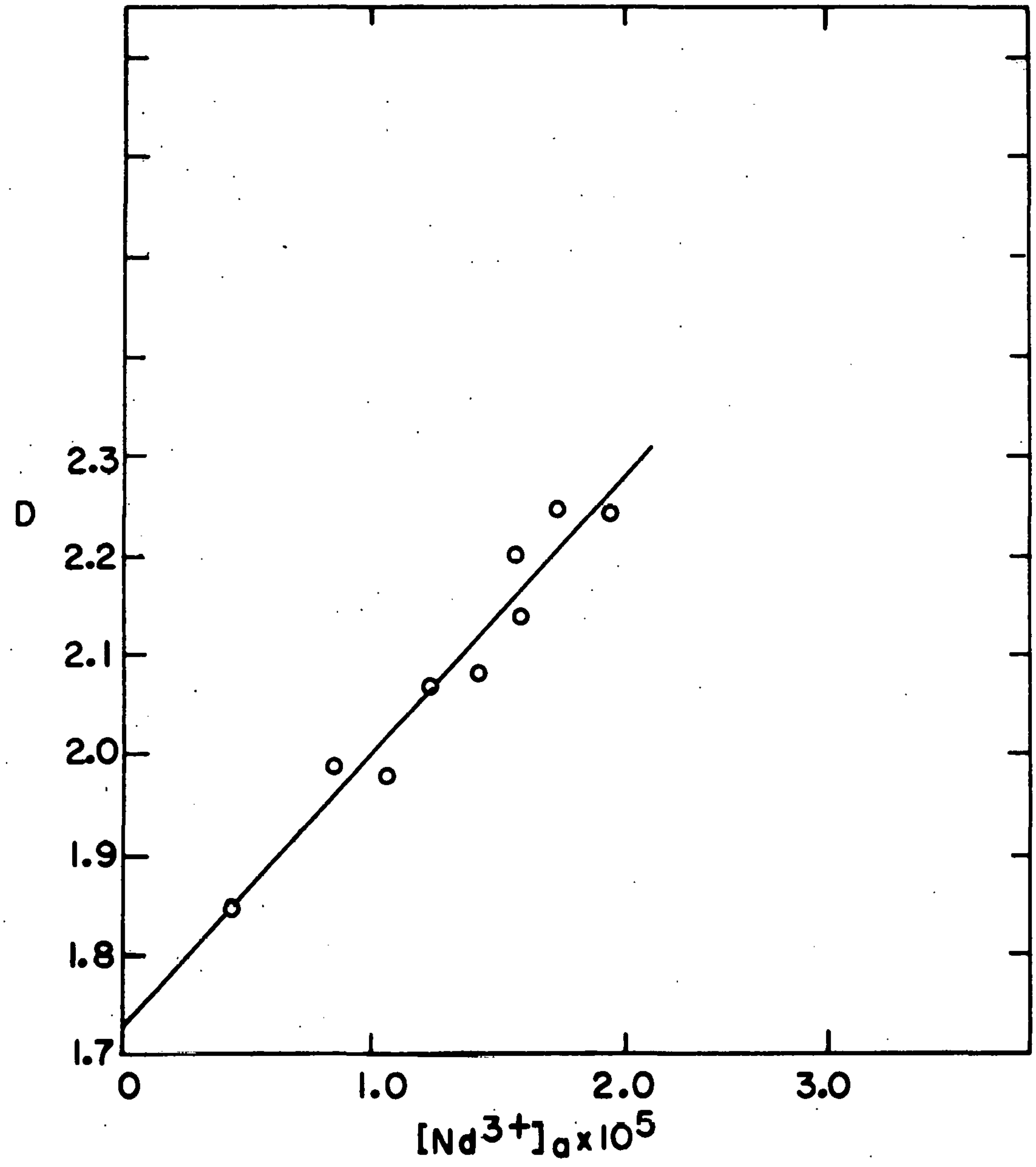


Figure 6. D as a function of aqueous neodymium concentration

simplification to a log-log plot was not a valid step. However, by performing additional experiments at low metal concentrations (where the amount of dimer present was very low), the log-log plots were again applicable and a value of 5 was still obtained for n.

In experiments performed in the absence of unionized acid, tracer-level neodymium extracted only to a slight extent. This small extraction severely limited the accurate determination of the distribution ratios. However, by working at higher metal concentrations, a trend in the dependence of D on $[M^{3+}]_a$ seemed to emerge. As $[M^{3+}]_a$ was increased, the extracting species changed from predominately a metal dimer to a more highly aggregated form.

The above data were compared to earlier extraction data taken at the same metal concentrations, but in the presence of unionized acid. The unionized acid containing species were found to constitute only a small fraction of the total metal extracted. This meant that the increased distribution at increased $[M^{3+}]_a$ could be chiefly attributed to a dimer containing some amount of unionized acid.

Thus, the extracting species at the tracer level are probably $MA_3(HA)_5$ and $(MA_3)_2(HA)_q$ plus small amounts of $(MA_3)_2$ and very small amounts of further aggregates $(MA_3)_J$. Any or all of these species may be hydrated to some extent.

One point of comparison should be made. As mentioned in an earlier chapter, Schweitzer and Sanghvi (54) studied the extraction of tracer-level thulium into chloroform using hexanoic acid. They determined the extracting species to be $TmA_3(HA)_5$. The identical stoichiometry of the tracer-level neodymium-DMHHA extracting species suggests that the two acids are behaving in a similar manner. This would imply that the DMHHA is binding in a nonchelating fashion and, hence, would not be expected to show any greatly increased selectivity.

The effect of ionic strength on tracer-level extraction was briefly examined and is shown in Figure 7. Unfortunately, the initial amount of HA, not the $(HA)_o$ concentration, was held constant, and so the effect observed was at least partially due to an increase in $[HA]_o$.

D. Additional Neodymium Extractions

Since the tracer-level experiments seemed to indicate an absence of unionized acid in the extracted dimer, an extraction of a macroscopic quantity of neodymium in the absence of unionized acid was attempted. Some extraction was observed, but the majority of the metal was precipitated at the phase interface. The withdrawal of most of the organic phase, followed by the introduction of fresh chloroform, caused an observable decrease in the amount of

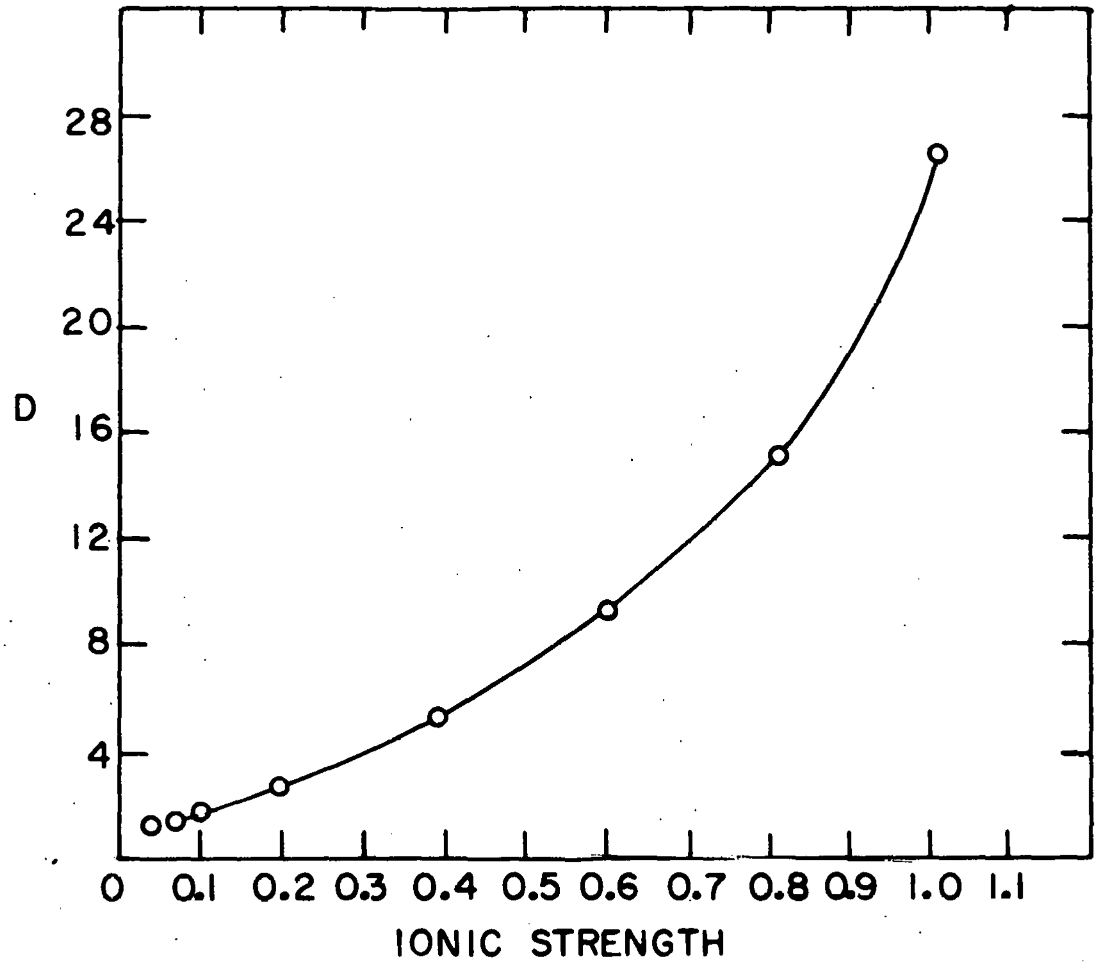


Figure 7. D as a function of ionic strength

precipitate present. With another repetition of this process, the remaining precipitate dissolved.

Analyses of the two organic phase portions which were removed, revealed a metal concentration in each of about 5×10^{-3} M. The final organic and aqueous phase metal concentrations were 2.9×10^{-3} M and 3.5×10^{-4} M, respectively. Both of the two organic aliquots were examined osmometrically and showed virtually no detectable species molarity, indicating aggregation of the extract. Also, the precipitate was assayed and found to contain about 22.7% neodymium, which would correspond to $NdA_3 \cdot H_2O$ (22.6%).

Thus, the neodymium was extracted by the DMHHA anion into chloroform, but had a solubility limit of about 5×10^{-3} M. The extract appeared to be extensively aggregated.

Addition of free acid to a neodymium-DMHHA anion solution caused the metal solubility in chloroform to increase. In a solution containing only metal and acid anion, the addition of unionized acid effected the dissolution of all the precipitate present. The final unionized acid to metal ratio was 0.5.

In another experiment, neodymium which was precipitated from an organic-free water solution containing only a 0.2/1 free acid to metal ratio, was subsequently dissolved in chloroform, and metal concentrations as high as 0.0211 M were obtained. Analysis of the precipitate revealed 20.65% neodymium. The $NdA_3 \cdot 4H_2O$ species would contain 20.8% neodymium, but a substance containing unionized acid would be more likely, since the previously mentioned precipitate formed only a monohydrate, and since the solubility of this precipitate was so high. A mono-hydrate species containing 20.65% neodymium would have the stoichiometry of $NdA_3 \cdot 0.37 HA \cdot H_2O$. Osmometry of the 0.0211 M (in metal) chloroform solution showed a species molarity of about 0.001, which indicated an average aggregation number $\geq$ 20.

In experiments involving unionized acid to metal ratios of greater than one, the metal was generally observed to extract rather immediately. However, upon standing over a period of several days to weeks, a large percentage of the metal precipitated from the organic phase. The rate of appearance of precipitate was directly related to the amount of unionized acid present.

Precipitate formed from a solution containing an acid-to-metal ratio of greater than sixteen was assayed and found to contain 15.05% neodymium. The best stoichiometric fit to this percentage would be $NdA_3 \cdot 2HA \cdot H_2O$ (15.04%). This would help to explain the appearance of some precipitate at unionized acid to metal ratios much over one. However, since metal carboxylate soaps frequently precipitate as non-stoichiometric substances (70), the above should be regarded more as an average composition than a definite molecular formula.

From the above extraction experiments and the earlier tracer work, some conclusions can be made regarding the extraction of neodymium. The extracting species can be represented as

$$MA_3(HA)_5 + \sum_{2}^{J} (MA_3)_J + \sum_{2}^{K} \sum_{1}^{M} (MA_3)_K(HA)_M$$

where $M < 2K$. This scheme is consistent with metal dependence, unionized acid enhancement of extraction and the nonnecessity of unionized acid to effect extraction. On a macroscopic scale, the metal becomes extensively aggregated to form micelles. The presence of too large an amount of unionized acid apparently alters the structure of the micelle, and causes the neodymium to precipitate.

E. Heavy Lanthanide Extractions

In the absence of an organic soluble cation, no significant extraction of the lanthanides past samarium was observed. The aqueous phase usually formed a cloudy but stable emulsion, accompanied by some precipitation at the phase interface.

It was thought that a possible reason for the divergent behavior of the heavy lanthanides might lie in an inability to form the aggregates apparently needed for extraction.

A similar example of distinction in aggregate formation, though distantly related, has been seen in the solid state structures of the lanthanide HEDTA complexes (71). The lanthanum through praseodymium complexes have all been determined to crystallize as dimers, with shared carboxylate oxygens. In contrast, the heavier lanthanides thus far examined have been found to crystallize as monomers, apparently due to spatial considerations.

To evaluate the heavy lanthanide-DMHHA aggregation in chloroform, some tracer-scale thulium extractions were performed. As with the neodymium tracer experiments, the dependence of the distribution ratio on the metal concentration was examined and the results are shown in Figure 8. A definite metal dependence is seen, indicating the formation of metal dimers. Presumably, further aggregation could occur at higher metal concentrations.

As a consequence of the above, the nonextractability of the heavy lanthanides remains to be attributed to one or both of two factors. The heavy lanthanide aggregates may be less soluble than their lighter lanthanide analogues, possibly due to a difference in structure. A second possibility is that the heavy lanthanide carboxylates are aggregating to a greater extent, causing a change in chloroform solubility. This latter explanation is consistent with the observation (72,73) that the aggregation

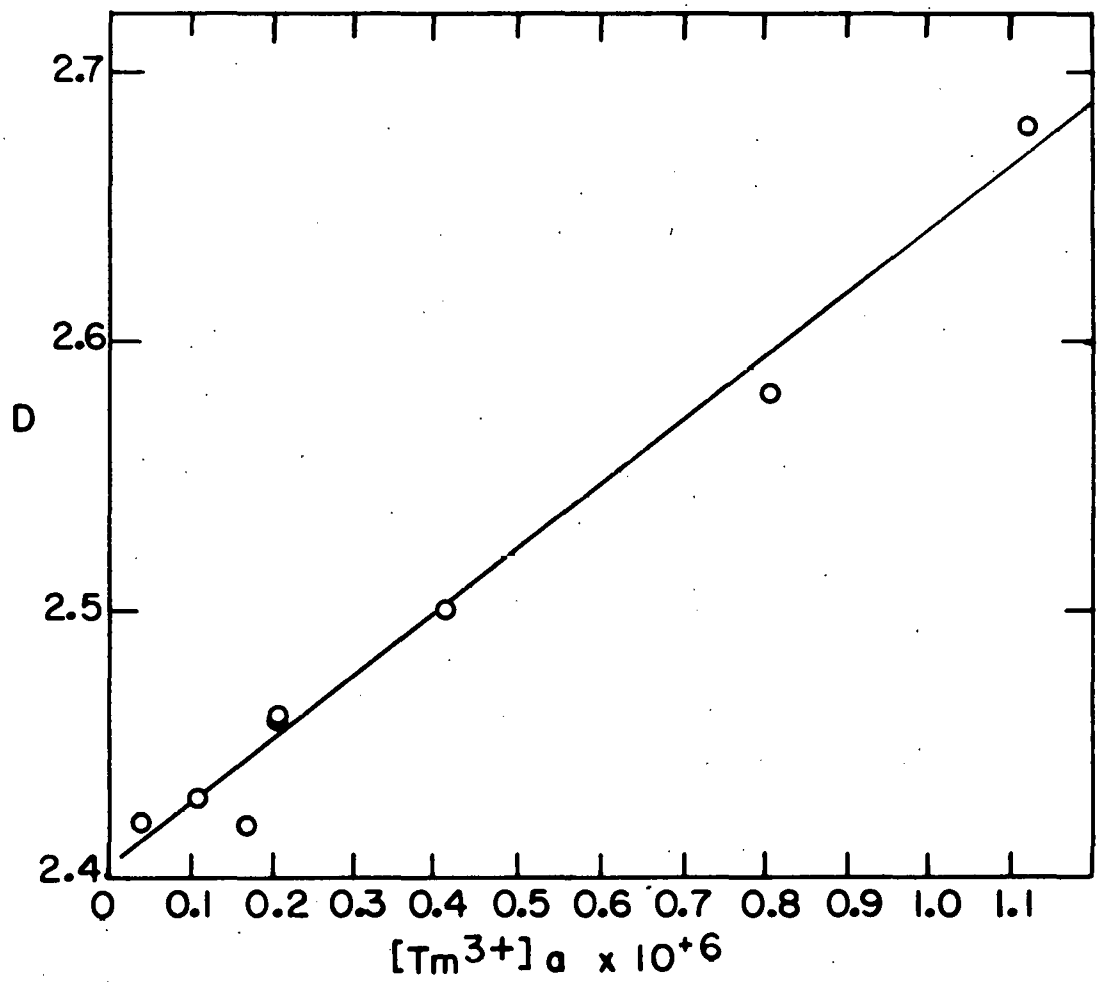


Figure 8. D as a function of aqueous thulium concentration

number of ionic surfactants increases with a decrease in the counter-ion radius.

When erbium extractions were performed using tetrabutyl ammonium hydroxide as the base for neutralizing the DMHHA, significant extraction was obtained. Apparently, the organic soluble tetrabutyl ammonium ion permitted the formation and extraction of ion pairs (e.g., $Bu_4N^+MA_4^-$). However, as with the neodymium extractions, an excess of free acid caused precipitation to occur.

F. Additional Lanthanide-DMHHA Stability Constants

Certain α-hydroxy carboxylic acids (74,75) have been found to exhibit interesting trends in their stability constants with the lanthanides. Instead of increasing monotonically with a decrease in the cationic radius, the stability constants rise to a maximum around samarium and then fall slightly before again rising for the heavier lanthanides. The lanthanide-DMHHA stability constants were obtained for the lanthanides below promethium. (The low solubility limits of the other lanthanide complexes prevented the measurement of their stability constants.) The results are shown in Table 3 and follow a normal trend.

Table 3. Lanthanide-DMHHA stability constants

Ln^{3+}	Nd	Pr	Ce	La
$\beta_1 \times 10^2$	4.71(.08)	3.39(.14)	2.91(.19)	2.06(.05)
$\beta_2 \times 10^4$	4.27(.33)	2.03(.28)	1.04(.27)	0.37(.08)
$\beta_3 \times 10^6$	1.64(.34)	1.38(.24)	0.52(.16)	0.30(.04)

G. Adjacent Lanthanide Separation Factors

The separation factors obtained from the lanthanide-DMHHA extractions are listed in Table 4. These are, in general, not too different from those reported for the normal aliphatic carboxylic acids (53,59). Little, if any, improvement can be seen. A possible explanation for the poor DMHHA separation factors has been discussed earlier. If the hydroxyl group is not participating in the bonding, then the

Table 4. Lanthanide-DMHHA separation factors

Lanthanide Pair	Ce/La	Pr/Ce	Nd/Pr	Sm/Nd
SF	1.2	1.4[a]	1.2,1.5[a]	1.8

[a] Estimated from distribution ratios.

DMHHA would be expected to behave much like a normal carboxylic acid, and would not produce any significant improvement in extraction selectivity.

VII. SUMMARY

A. Conclusions

DMHHA distributes between water and chloroform with a partition coefficient of about one (at 0.1 M ionic strength and 25°C). The acid dimerizes in chloroform, and, at higher acid concentrations aggregates even further.

The light lanthanides can be extracted into chloroform by forming complexes with the DMHHA anions. The extracted metal species is highly aggregated. This extraction has a solubility limit which increases with the addition of unionized acid. The resultant extract is also highly aggregated. As the unionized acid to metal ratio begins to exceed one, extraction at first occurs, followed by the slow precipitation of $MA_3 \cdot 2HA \cdot H_2O$.

At the tracer level, neodymium is extracted primarily as $NdA_3 \cdot (HA)_5$ and $NdA_3 \cdot (HA)_q$. Very small amounts of $(NdA_3)_2$ and other metal aggregates are also present.

The heavy lanthanides do not extract from solutions of DMHHA and its potassium salt. Precipitates and aqueous emulsions are formed instead. This is presumably due to the formation of larger, but less soluble aggregates. The heavy lanthanides can be extracted from solutions containing DMHHA and the organic-soluble tetrabutyl ammonium ion. The metals are probably extracted as ion pairs.

The separation factors obtained from DMHHA extractions of the light lanthanides are comparable to those obtained in extractions employing normal aliphatic carboxylic acids. The lack of improvement can be attributed to an inability of the hydroxy group to participate in the bonding.

B. Future Work

In retrospect, the choice of chloroform as the solvent for extraction was an unfortunate one. The aggregation of the extracted metal and the number of different species formed make analyses very difficult. The solubility restrictions on the acid to metal ratio, coupled with mediocre separation factors, virtually eliminate any separations application.

Extractions into hexanol look promising. Both the light and heavy lanthanides have been found to extract almost quantitatively. Unionized acid to metal ratios of greater than 10/1 are needed before precipitation begins. Another significant factor is the higher dielectric constant of hexanol (13.3 compared to a value of 4.81 for chloroform). This means that the extracted metal would not need to be as highly shielded from the more polar hexanol molecules. This, in turn, would reduce the tendency of the extract to aggregate or to bind additional unionized acid molecules. In fact, the alcoholic ends of the hexanol molecules could themselves help to solvate the metal ion. Finally, the DMHHA could presumably coordinate in a chelating fashion and yield improved separation factors.

The examination of the lanthanide extraction behavior with other α-hydroxy acids might prove interesting. Knowing the effect of carbon number and chain branching could be useful in designing the optimum extracting agent. Dihydroxy acids, which have the potential to show greater selectivities, could also be the focus of extraction experiments.

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X. APPENDIX A: COMPUTER PROGRAM ALFA

```
C
C                 PROGRAM ALPHA
C
C     THIS PROGRAM IS DESIGNED TO CALCULATE SAMPLE KNO3 VOLUMES FOR RUNS
C     DETERMINING LIGAND PROTONATION CONSTANTS USING TRIAL ALPHAS FOR ANY
C     POLYBASIC LIGAND
C     APPROXIMATION IS USED IN VARIABLE OTHER
C  ***********************DATA SET MAKEUP ********************************
C     CARD   VARIABLE  COL  FORMAT            EXPLANATION
C    ------------------------------------------------------------------
C      1       TITE   1-80     A80     ANY TITLE
C      2          N    1-5      I5     NUMBER OF DATA POINTS
C                NN     10      I1     NUMBER OF ALPHAS INPUT
C              HTIT     15      I1     NUMBER OF TITRATABLE H PER LIGAND
C             CACID  21-30   F10.4     MOLARITY OF LIGAND ACID SOLN
C             CBASE  31-40   F10.4     MOLARITY OF BASE SOLN
C             CHNO3  41-50   F10.4     MOLARITY OF STRONG ACID SOLN
C              FINV  51-60   F10.4     FINAL VOLUME
C             CKNO3  61-70   F10.4     MOLARITY OF KNO3 SOLN
C                US  71-80   F10.4     IONIC STRENGTH DESIRED
C      3  ALPHA(I)    1-10   E10.4     1 TO NN ASSUMED ALPHAS USED, ONE
C                                        PER CARD
C      4  VACID(I)    1-10   F10.5     VOLUME OF LIGAND ACID SOLN USED
C         VEASE(I)   11-20   F10.5     VOLUME OF BASE SOLN USED
C         VHNO3(I)   21-30   F10.5     VOLUME OF STRONG ACID SOLN USED
C    (REPEAT UNTIL I=N)
      DIMENSION ALPHA(6),VACID(100),VBASE(100),VHNO3(100),TITE(20),CNBAR
     1(100),APH(100),VKNO3(100)
      INTEGER HTIT
      DOUBLE PRECISION BOT,TOP,OTHER,UA
      READ(5,1)(TITE(I),I=1,20)
      READ(5,2)N,NN,HTIT,CACID,CBASE,CHNO3,FINV,CKNO3,US
      READ(5,3)(ALPHA(I),I=1,NN)
      READ(5,4)(VACID(I),VBASE(I),VHNO3(I),I=1,N)
      ERR=0.001
```

```
      DO 100 M=1,N
      AT=(CACID/FINV)*VACID(M)
      HT=(CACID/FINV)*VACID(M)*HTIT+(CHNO3/FINV)*VHNO3(M)-(CBASE/FINV)*
     1VBASE(M)
      H=0.0
      HFAC=10.0
   10 HINC=HT/HFAC
   20 H=H+HINC
      HPH=-ALOG10(H)
      ANBAR=(HT-H+10**(-13.8069+HPH))/AT
      BOT=1.0
      TOP=0.0
      DO 40 K=1,NN
      BOT=BOT+ALPHA(K)*H**K
      TOP=TOP+K*ALPHA(K)*H**K
   40 CONTINUE
      BNBAR=TOP/BOT
      TEST=ANBAR-BNBAR
      IF(ABS(TEST).LE.ERR) GO TO 70
      IF(TEST.GT.0.0) GO TO 20
      H=H-HINC
      HFAC=HFAC*10
      GO TO 10
   70 CONTINUE
      A=AT/BOT
      CNBAR(M)=BNBAR
      APH(M)=-ALOG10(H)
      OTHER=(HTIT)**2*A*.5
      DO 80 K=1,NN
      OTHER=OTHER+(K-HTIT)**2*ALPHA(K)*H**K*A*.5
   80 CONTINUE
      UA=.5*(CBASE/FINV)*VBASE(M)+.5*(CHNO3/FINV)*VHNO3(M)+OTHER
     1+.5/10.0**APH(M)+.5*10.0**(-13.8069+APH(M))
      VKNO3(M)=((US-UA)/CKNO3)*FINV
  100 CONTINUE
```

```
     WRITE(6,200)
     WRITE(6,201)(TITE(I),I=1,20)
     WRITE(6,202)CACID,CBASE
     WRITE(6,203)CHNO3,CKNO3
     WRITE(6,204)FINV,US
     WRITE(6,205)
     WRITE(6,206)(L,VACID(L),VBASE(L),VHNO3(L),APH(L),CNBAR(L),VKNO3(L)
    1,L=1,N)
     WRITE(6,207)NN
     WRITE(6,208)(IW,ALPHA(IW),IW=1,NN)
   1 FORMAT(20A4)
   2 FORMAT(I5,4X,I1,4X,I1,5X,6F10.4)
   3 FORMAT(E10.4)
   4 FORMAT(3F10.5)
 200 FORMAT('1******************TRIAL CALCULATION OF VKNO3 FROM ASSUMED
    1 ALPHAS****************************'/)
 201 FORMAT(' ',20A4/)
 202 FORMAT(T2,'ORIGINAL ACID CONCENTRATION =',T40,F8.5,T55,'ORIGINAL B
    1ASE CONCENTRATION =',T90,F8.5)
 203 FORMAT(T2,'ORIGINAL STRONG ACID CONCENTRATION =',T40,F8.5,T55,
    1'POTASSIUM NITRATE CONCENTRATION =',T90,F8.5)
 204 FORMAT(T2,'FINAL VOLUME =',T39,F7.3,T55,'IONIC STRENGTH =',T90,
    1F8.5/)
 205 FORMAT('   (I)',T9,'VACID',T19,'VBASE',T29,'VHNO3',T41,
    1'PH',T48,'NBAR',T56,'VCL KNO3')
 206 FORMAT(' ',I3,T8,F7.3,T18,F7.3,T28,F7.3,T38,F7.4,T48,F6.3,T58,
    1F7.3)
 207 FORMAT('0ASSUMED PROTONATION CONSTANTS  ALPHA(1)-ALPHA(',I2,')'/)
 208 FORMAT(6X,I2,6X,E12.5)
     RETURN
     END
```

XI. APPENDIX B: COMPUTER PROGRAM BETA

```
C
C                 PROGRAM BETA
C
C    THIS PROGRAM IS DESIGNED TO CALCULATE SAMPLE KNC3 VOLUMES FOR RUNS
C    DETERMINING STABILITY CCNSTANTS,USING KNOWN ALPHAS AND ASSUMED BETAS
C
C ********************** DATA SET MAKEUP ********************************
C    CARD   VARIABLE  COL  FCRMAT              EXPLANATION
C   ------------------------------------------------------------------
C      1       TITE   1-80    A80      ANY TITLE
C      2      VACID   1-10   F10.5     VOLUME OF LIGAND ACID SOLN USED
C             CACID  11-20   F10.5     MOLARITY OF LIGAND ACID SOLN USED
C              VMET  21-30   F10.5     VOLUME OF METAL SOLN USED
C              CMET  31-40   F10.5     MOLARITY OF METAL SOLN
C              CKNO  41-50   F10.5     MOLARITY OF KNO3 SOLN
C             CBASE  51-60   F10.5     MOLARITY OF BASE SOLN
C              FINV  61-70   F10.5     FINAL VOLUME
C                US  71-80   F10.5     IONIC STRENGTH DESIRED
C      3          N    1-5      I5     NUMBER OF DATA POINTS
C                NN     10      I5     NUMBER OF BETAS INPUT
C               NNN     15      I5     NUMBER OF ALPHAS INPUT
C              HTIT     20      I5     NUMBER OF TITRATABLE H PER LIGAND
C                ZC     25      I5     CHARGE ON METAL CATION
C                ZA     30      I5     CHARGE ON LIGAND ANION
C      4   ALPHA(I)   1-10   E10.4     1 TO NNN ALPHAS USED,ONE PER CARD
C      5    BETA(I)   1-10   E10.4     1 TO NN ASSUMED BETAS USED, ONE
C                                        PER CARD
C      6   VEASE(I)   1-80   F10.4     1 TO N BASE VOLUMES USED, EIGHT
C                                        PER CARD
C
      DIMENSION TITE(20),ALPHA(6),BETA(5),VBASE(50),CNBAR(50),APH(50),
     1VKNO(50)
      REAL MT
      INTEGER HTIT,ZC,ZA
    9 READ(5,1,END=300)(TITE(IR),IR=1,20)
```

```
      READ(5,2)VACID,CACID,VMET,CMET,CKNO,CBASE,FINV,US
      READ(5,3)N,NN,NNN,HTIT,ZC,ZA
      READ(5,4)(ALPHA(I),I=1,NNN)
      READ(5,4)(BETA(I),I=1,NN)
      READ(5,5)(VBASE(I),I=1,N)
      ERR=0.001
      MT=(CMET/FINV)*VMET
      AT=(CACID/FINV)*VACID
      DO 100 M=1,N
      HT=(CACID/FINV)*VACID*HTIT-(CBASE/FINV)*VBASE(M)
      H=0.0
      HFAC=10.0
   10 HINC=HT/HFAC
   20 H=H+HINC
      ALPTO=0.0
      DO 30 I=1,NNN
   30 ALPTO=ALPTO+ALPHA(I)*I*H**I
      A=(HT-H)/ALPTO
      BOT=1.0
      TOP=0.0
      DO 40 K=1,NN
      BOT=BOT+BETA(K)*A**K
   40 TOP=TOP+K*BETA(K)*A**K
      BNBAR=TOP/BOT
      ALFTO=1.0
      DO 50 J=1,NNN
   50 ALFTO=ALFTO+ALPHA(J)*H**J
      ANBAR=(AT-A*ALFTO)/MT
      TEST=ANBAR-BNBAR
      IF(ABS(TEST).LE.ERR)GO TO 70
      IF(TEST.LT.0.0) GO TO 20
      H=H-HINC
      HFAC=HFAC*10.
      GO TO 10
   70 CONTINUE
```

```
      CNBAR(M)=BNBAR
      APH(M)=-ALOG10(H)
      OTHER=(HTIT)**2*A
      DO 80 K=1,NNN
      OTHER=OTHER+(K-HTIT)**2*ALPHA(K)*H**K*A
   80 CONTINUE
      UA=0.5*OTHER
      UB=0.5*CBASE*VBASE(M)/FINV
      UC=0.5*10.0**(-APH(M))
      UD=0.5*10.0**(-13.8069+APH(M))
      UE=0.5*ZC*MT
      UF=0.5*MT*(ZC-BNBAR*ZA)**2
      UA=UA+UB+UC+UD+UE+UF
      VKNO(M)=((US-UA)/CKNO)*FINV
  100 CONTINUE
      WRITE(6,199)
      WRITE(6,200)
      WRITE(6,201)(TITE(I),I=1,20)
      WRITE(6,202)CACID
      WRITE(6,203)CMET
      WRITE(6,204)CBASE
      WRITE(6,205)CKNO
      WRITE(6,212)VACID
      WRITE(6,213)VMET
      WRITE(6,214)US
      WRITE(6,215)FINV
      WRITE(6,206)
      WRITE(6,207)(L,VBASE(L),APH(L),CNBAR(L),VKNO(L),L=1,N)
      WRITE(6,208)(IW,ALPHA(IW),IW=1,NNN)
      WRITE(6,209)(IX,BETA(IX),IX=1,NN)
      GO TO 9
  300 STOP
    1 FORMAT(20A4)
    2 FORMAT(8F10.5)
    3 FORMAT(6I5)
```

```
  4 FORMAT(E10.4)
  5 FORMAT(8F10.4)
199 FORMAT('1**  TRIAL CALCULATION OF VKNO3 FROM **')
200 FORMAT(T2,'**  KNOWN ALPHAS AND ASSUMED BETAS  **'/)
201 FORMAT(' ',20A4/)
202 FORMAT(T2,'ORIGINAL  ACID CONCENTRATION =',T35,F8.5)
203 FORMAT(T2,'ORIGINAL METAL CONCENTRATION =',T35,F8.5)
204 FORMAT(T2,'ORIGINAL MEASE CONCENTRATION =',T35,F8.5)
205 FORMAT(T2,'ORIGINAL MKNO3 CONCENTRATION =',T35,F8.5)
212 FORMAT(T2,'VOLUME OF ACID SOLN USED =',T35,F8.5)
213 FORMAT(T2,'VOLUME OF METAL SOLN USED =',T35,F8.5)
214 FORMAT(T2,'IONIC STRENGTH =',T35,F8.5)
215 FORMAT(T2,'FINAL VOLUME =',T35,F7.3/)
206 FORMAT(' (I)',T9,'VBASE',T21,'PH',T30,'NBAR',T36,'VOL KNO3')
207 FORMAT(' ',I3,T8,F7.3,T18,F7.4,T28,F6.3,T38,F6.3)
208 FORMAT('0','ALPHA(',I1,') =',4X,E12.5)
209 FORMAT('0','BETA(',I1,') =',5X,E12.5)
    RETURN
    END
```

XII. APPENDIX C: COMPUTER PROGRAM OMEGA

```
C
C                   PROGRAM OMEGA
C
C  ********************DATA SET MAKEUP**************************************
C     CARD  VARIABLE  COL  FORMAT              EXPLANATION
C    ---------------------------------------------------------------------------
C       1          N    1-3     I3       NUMBER OF DATA POINTS
C                 NN      5     I1       NUMBER OF COSTANTS TO BE DETERMINED
C               IFUN      6     I1       OPTION TO BE USED
C                                        =1 CALCULATE KNO3 VOL FOR STABILITY
C                                           CONSTANTS BASED ON TRIAL PH
C                                        =2 CALCULATION OF PROTONATION
C                                           CONSTANTS(ALPHAS)
C                                        =3 CALCULATION OF STABILITY CONSTANTS
C                                           (BETAS)
C              BETA1   8-17  E10.4       IF IFUN=2,BETAS ARE ALL SET TO ZERO
C              BETA2  18-27  E10.4
C              BETA3  28-37  E10.4
C              BETA4  38-47  E10.4
C              BETA5  48-57  E10.4
C               HTIT     60     I1       NUMBER OF TITRATABLE H PER LIGAND
C                 ZC     65     I1       CHARGE ON METAL CATION,=0 IF IFUN=2
C                 ZA     70     I1       CHARGE ON LIGAND ANION,=0 IF IFUN=2
C       2      TITLE   1-80    A80       ANY TITLE
C       3      CACID   1-10  F10.5       MOLARITY OF LIGAND ACID SOLN
C              CBASE  11-20  F10.5       MOLARITY OF BASE SOLN
C               CHCL  21-30  F10.5       MOLARITY OF STRONG ACID
C               FINV  31-40  F10.5       FINAL VOLUME
C               CKNO  41-50  F10.5       MOLARITY OF KNO3
C                 US  51-60  F10.5       IONIC STRENGTH DESIRED
C               VMET  61-70  F10.5       VOLUME OF METAL SOLN USED
C               CMET  71-80  F10.5       MOLARITY OF METAL SOLN
C       4   VACID(I)   1-10  F10.5       VOLUME OF LIGAND ACID SOLN USED
C           VBASE(I)  11-20  F10.5       VOLUME OF BASE SOLN USED
C            VHCL(I)  21-30  F10.5       VOLUME OF STRONG ACID SOLN USED
```

```
C          HPH(I)  31-40  F10.5      MEASURED PH
C    (REPEAT  UNTIL I=N)
C     N+4     RELAT   1-10  F10.5      RELATIVE ERROR IN ATOT
C             RELHT  11-20  F10.5      RELATIVE ERROR IN HTOT
C             RELPH  21-30  F10.5      RELATIVE ERROR IN PH
C             IWEIT  39-40     I2      WEIGHTING OPTION TO BE USED FOR DATA
C                                      =-1 WEIGHTING DONE USING ATOT,
C                                         HTOT, AND PH
C                                      =0 WEIGHTING ON PH ONLY
C                                      =1 NO WEIGHTING OF DATA
C     N+5     ALFA1   1-10  E10.4      USED ONLY IF IFUN=3
C             ALFA2  11-20  E10.4
C             ALFA3  21-30  E10.4
C             ALFA4  31-40  E10.4
C             ALFA5  41-50  E10.4
C             ALFA6  51-60  E10.4
C
C    ..................................................................
C       SUBROUTINE DGELG
C          PROGRAM SUPPLIED BY COMPUTER
C
C       PURPOSE
C          SOLVE GENERAL SYSTEM OF SIMULTAEOUS LINEAR EQUATIONS
C
C       USAGE
C          CALL DGELG(R,A,M,N,EPS,IER)
C
C       DESCRIPTION OF PARAMETERS
C          R - DOUBLE PRECISION M BY N RIGHT HAND SIDE MATRIX(DESTROYED)
C              ON RETURN CONTAINS SOLUTIONS OF THE EQUATIONS
C          A - DOUBLE PRECISION M BY N COEFFICIENT MATRIX (DESTROYED)
C          M - NUMBER OF EQUATIONS IN SYSTEM
C          N - NUMBER OF RIGHT HAND SIDE VECTORS
C          EPS - SINGLE PRECISION INPUT CONSTANT USED AS RELATIVE
C                TOLERANCE FOR TEST ON LOSS OF SIGNIFICANCE
```

```
C           IER=0 - NO ERROR
C           IER=-1 - NO RESULT DUE TO M LESS THAN 1, OR PIVOT ELEMENT AT
C                    ANY ELIMINATION STEP EQUAL TO 0
C           IER=5 - WARNING DUE TO POSSIBLE LOSS OF SIGNIFICANCE
C                   INDICATED AT ELIMINATION STEP K+1 WHERE PIVOT ELEMENT
C                   WAS LESS THAN OR EQUAL TO INTERNAL TOLERANCE EPS
C                   TIMES ABSOLUTELY GREATEST ELEMENT OF MATRIX A
C
C        REMARKS
C           SEE IBM BULLETIN
C
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C           NONE
C
C        METHOD
C           SOLUTION IS DONE BY GAUSS-ELIMINATION WITH COMPLETE PIVOTING
C
C     ..................................................................
C
      DIMENSION TITLE(20),VACID(100),VBASE(100),VHCL(100),
     1HPH(100),ETA(100),PERCE(100),AK(4),PK(4),VKNO3(100),BETAN(6),
     &XTX(36),SXTX(36)
      INTEGER HTIT,ZA,ZC
      COMMON /TRID/ X(100),Y(100),Z(100),BETA(6),N,NN,IER,
     1PHI(100),E(100),VBETA(6),RELAT,RELHT,RELPH,IWEIT,IFUN,ALFA(6),
     &CH(100)
      DOUBLE PRECISION Q(100,6),XTX
      ITEST=0                                                           0440
  250 READ(5,1,END=300) N,NN,IFUN,BETA(1),BETA(2),BETA(3),BETA(4),
     &BETA(5),HTIT,ZC,ZA
      READ(5,2)(TITLE(I),I=1,20)
      READ(5,3)CACID,CBASE,CHCL,FINV,CKNO,US,VMET,CMET
      READ(5,4)(VACID(I),VBASE(I),VHCL(I),HPH(I),I=1,N)
      READ(5,6)RELAT,RELHT,RELPH,IWEIT
      IF (IFUN.EQ.3)  READ(5,5)(ALFA(I),I=1,6)
```

```
      DO 30 I=1,N
      IF (IFUN.EQ.3) GO TO 18
      Z(I)=(VACID(I)/FINV)*CACID
      X(I)=1.0/10.0**HPH(I)
      Y(I)=HTIT*(VACID(I)/FINV)*CACID+(VHCL(I)/FINV)*CHCL
     1-(VBASE(I)/FINV)*CBASE+10.0**(-13.8069+HPH(I))
      GO TO 19
   18 CONTINUE
      CH(I)=1./10.**HPH(I)
      BH=CH(I)
      Z(I)=VMET/FINV*CMET
      Y(I)=VACID(I)*CACID/FINV
      X(I)=(HTIT*Y(I)-VBASE(I)/FINV*CBASE-BH)/(ALFA(1)*BH+2.*ALFA(2)*
     &BH**2+3.*ALFA(3)*BH**3+4.*ALFA(4)*BH**4+5.*ALFA(5)*BH**5+
     &6.*ALFA(6)*BH**6)
      Y(I)=VACID(I)/FINV*CACID-X(I)*(ALFA(1)*BH+ALFA(2)*BH**2+ALFA(3)*
     &BH**3+ALFA(4)*BH**4+ALFA(5)*BH**5+ALFA(6)*BH**6)
   19 CONTINUE
      ETA(I)=(Y(I)-X(I))/Z(I)
   30 CONTINUE
   20 CONTINUE
      IF (IFUN.NE.1) CALL CFIT(Q,XTX,SXTX)
      DO 40 I=1,N
C  DON'T GET EXCITED, JUST USING PERCE HERE TO SAVE CORE
      PERCE(I)=1.0
      PHI(I)=0.0
      DO 45 K=1,NN
      PHI(I)=PHI(I)+K*BETA(K)*X(I)**K
      PERCE(I)=PERCE(I)+BETA(K)*X(I)**K
   45 CONTINUE
      PHI(I)=PHI(I)/PERCE(I)
      PERCE(I)=(ETA(I)-PHI(I))/PHI(I)*100.0
   40 CONTINUE
      IF (NN.EQ.1) GO TO 61
      NM=NN-1
```

```
      DO 60 I=1.NM
      AK(I)=BETA(NN-I)/BETA(NN-I+1)
      IF (AK(I).LE.0.0) PK(I)=0.0
      IF (AK(I).GT.0.0) PK(I)=-ALOG10(AK(I))
   60 CONTINUE
   61 CONTINUE
      AK(NN)=1.0/BETA(1)
      IF (AK(NN).GT.0.0) PK(NN)=-ALOG10(AK(NN))
      IF (AK(NN).LE.0.0) PK(NN)=0.0
      IF (IFUN.LE.2) GO TO 83
      DO 41 I=1.N
      UA=.5*(VBASE(I)*CBASE/FINV+VHCL(I)*CHCL/FINV+
     &ZC*VMET*CMET/FINV+CH(I)+X(I)*ZA**2+X(I)*(ALFA(1)*(ZA-1)**2*CH(I)+
     1ALFA(2)*CH(I)**2*(ZA-2)**2+ALFA(3)*CH(I)**3*(ZA-3)**2+ALFA(4)*
     2CH(I)**4*(ZA-4)**2+ALFA(5)*CH(I)**5*(ZA-5)**2+ALFA(6)*CH(I)**6*
     3(ZA-6)**2)+Z(I)*(ZC-PHI(I)*ZA)**2)
      VKNO3(I)=(US-UA)*FINV/CKNO
   41 CONTINUE
   83 CONTINUE
      IF (IFUN.GT.2)  GO TO 47
      DO 42 IS=1.N
      UA=.5*(VBASE(IS)/FINV)*CBASE+.5*(VHCL(IS)/FINV)*CHCL
     1+.5/10.0**HPH(IS)+.5*(VACID(IS)/FINV)*CACID*
     2(HTIT-PHI(IS))**2+0.5*10**(-13.8069+HPH(IS))
      VKNO3(IS)=((US-UA)/CKNO)*FINV
   42 CONTINUE
   47 CONTINUE
      IF (IFUN.EQ.1)WRITE(6,98)
      WRITE(6,101)(TITLE(I),I=1,20)
      WRITE(6,102)CACID,CBASE
      WRITE(6,103)CHCL,CKNO
      WRITE(6,110)FINV,US
      WRITE(6,108)CMET,VMET
      WRITE(6,104)
      WRITE(6,105)(I,VACID(I),VBASE(I),VHCL(I),HPH(I),
```

```
     1ETA(I),PERCE(I),VKNO3(I),E(I),I=1,N)
      IF(NN.EQ.1) GO TO 48
      GO TO 49
   48 WRITE(6,111)
      WRITE(6,109)(I,BETA(I),AK(I),PK(I),I=1,NN)
      GO TO 50
   49 WRITE(6,106)
      WRITE(6,107)(I,BETA(I),AK(I),PK(I),VBETA(I),I=1,NN)
      WRITE(6,112)IWEIT
  112 FORMAT('0',5X,'WEIGHTING OPTION USED =',3X,I2)
   50 CONTINUE
      GO TO 250                                                         03090
  300 STOP
  102 FORMAT (T2,'ORIGINAL ACID CONCENTRATION =',T40,F8.5,T50,
     1'ORIGINAL BASE CONCENTRATION = ',T90,F8.5)
  101 FORMAT (20A4)
  103 FORMAT (T2,'ORIGINAL STRONG ACID CONCENTRATION = ',T40,
     1F8.5,T50,'POTASSIUM NITRATE CONCENTRATION =',T90,F8.5)
  110 FORMAT (T2,'FINAL VOLUME =',T40,F7.3,T50,'IONIC STRENGTH =',T90,
     1F7.3)
  104 FORMAT ('  (I)',T9,'VACID',T19,'VBASE',T29,'VHCL',T40
     1,'P(H)',T48,'NBAR',T58,'ERROR',T66,'VOL KNO3')
  105 FORMAT (' ',I3,T8,F7.3,T18,F7.3,T28,F7.3,T38,F7.4,T48,
     1F6.3,T58,F7.2,T68,F6.3,T78,F6.3)
  106 FORMAT (T7,'(I)',T15,'BETA(I)',T30,'K(I)',T40,'PK(I)',T55,
     1'VBETA(I)')
  107 FORMAT (T8,I2,T12,E12.4,T26,E12.4,T40,F6.3,T53,E12.5)
  108 FORMAT(T2,'METAL CONCENTRATION= ',T40,F8.5,T50,'METAL VOLUME =',
     &T90,F6.3)
  109 FORMAT(T8,I2,T12,E12.4,T26,E12.4,T40,F6.3)
  111 FORMAT (T7,'(I)',T15,'BETA(I)',T30,'K(I)',T40,'PK(I)')
   98 FORMAT('1******************************************** KNO3 CALCULA
     &TION ************************************')
    1 FORMAT(I3,1X,2I1,1X,5E10.4,2X,I1,4X,I1,4X,I1)
    2 FORMAT(20A4)
```

```
  3 FORMAT(8F10.5)
  4 FORMAT(4F10.5)
  5 FORMAT (6E10.4)
  6 FORMAT(3F10.5,8X,I2)
    END
    SUBROUTINE CFIT (Q,XTX,SXTX)
    COMMON /TRID/ X(100),Y(100),Z(100),BETA(6),N,NN,IER,
   1PHI(100),E(100),VBETA(6),RELAT,RELHT,RELPH,IWEIT,IFUN,ALFA(6),
   &CH(100)
    DIMENSION XT(600),EA(100),EH(100),EP(100),ET(100),YT(100),
   &XTX(NN,NN),BETAN(6),SXTX(NN,NN),LI(10),MI(10)
    DOUBLE PRECISION V(100),Q(N,NN),W(100),YT,XT,SST,
   &XTX,SSR,BETAN,XBETA(100)
    WRITE(6,1)NN
    DO 45 II=1,10
    DO 29 I=1,N
    SIGAT=0.0
    SIGHT=-1.0
    SIGPH=1.0
    DO 70 M=1,NN
    SIGPH=SIGPH-M*(Y(I)-X(I)-M*Z(I))*X(I)**(M-1)*BETA(M)+
   1X(I)**M*BETA(M)
    SIGHT=SIGHT-X(I)**M*BETA(M)
    SIGAT=SIGAT+M*X(I)**M*BETA(M)
 70 CONTINUE
    IF(IFUN.NE.3)GO TO 370
    SIGA=0.0
    DO 470 MM=1,5
    SIGA=SIGA+CH(I)**MM*X(I)*ALFA(MM)
470 CONTINUE
    SIGAP=1.+SIGA
    DO 570 JJ=1,NN
    SIGAP=SIGAP-JJ*(Y(I)-X(I)-JJ*Z(I))*X(I)**(JJ-1)*BETA(JJ)+
   &(1.+SIGA)*X(I)**JJ*BETA(JJ)
570 CONTINUE
```

```
      SIGPH=SIGAP
  370 CONTINUE
      EA(I)=SIGAT*RELAT*Z(I)
      EH(I)=SIGHT*RELHT*Y(I)
      EP(I)=SIGPH*RELPH*X(I)
      IF(IWEIT)71,72,73
   71 ET(I)=EA(I)+EP(I)+EH(I)
      GO TO 75
   72 ET(I)=EP(I)
      GO TO 75
   73 ET(I)=1.0
   75 CONTINUE
      DO 27 J=1,NN
      W(I)=1./ET(I)**2
  302 V(I)=X(I)-Y(I)
  303 Q(I,J)=(Y(I)-X(I)-J*Z(I))*X(I)**J
   27 CONTINUE
   29 CONTINUE
      IF (NN.NE.1) GO TO 40
      SUMQ=0.0
      SUMV=0.0
      DO 39 I1=1,N
      SUMQ=SUMQ+Q(I1,1)*W(I1)
      SUMV=SUMV+V(I1)*W(I1)
   39 CONTINUE
      BETA(1)=SUMV/SUMQ
      GO TO 50
   40 CALL WLSQ (Q,V,BETA,W,N,NN,XT)
   50 CONTINUE
   45 CONTINUE
      IF (NN.NE.1)  GO TO 60
      DO 59 I=1,N
      TEM=V(I)/Q(I,1)
      IF (TEM.LE.0.) TEM=1.
      E(I)=ALOG10(TEM)
```

```
   59 CONTINUE
      GO TO 80
   60 DO 90 J=1,NN
   90 BETAN(J)=BETA(J)
      CALL DGMTRA(V,YT,N,1)
      DO 99 I=1,N
   99 YT(I)=YT(I)*W(I)
      CALL DGMPRD(YT,V,SST,1,N,1)
      CALL DGMPRD(G,BETAN,XBETA,N,NN,1)
      CALL DGMPRD(YT,XBETA,SSR,1,N,1)
      CALL DGMPRD(XT,Q,XTX,NN,N,NN)
      SS=SNGL((SST-SSR)/(N-NN))
       WRITE(6,381 )SS,SSRD,SST,SSR
      DO 91 J=1,NN
      DO 92 L=1,NN
      SXTX(J,L)=SNGL(XTX(J,L))
   92 CONTINUE
   91 CONTINUE
      CALL MINV(SXTX,NN,D,LI,MI)
      DO 61 M=1,NN
      VBETA(M)=SQRT(SXTX(M,M)*SS)
   61 CONTINUE
      DO 94 I=1,N
   94 E(I)=10**9
   80 RETURN
  381 FORMAT(' ',5X,'MSE=',E10.4,5X,'MSR=',E10.4,5X,'SST=',E10.4,5X,'SSR
     &=',E10.4)
    1 FORMAT ('1*********************************************',I2,'PAR
     1AMETER PROGRAM USED**********************************')
      END
      SUBROUTINE WLSQ (X,Y,BETA,W,N,NN,XT)
      DIMENSION XT(600),XTX(36),DETA(6),X(1),Y(1),W(1),BETA(1),
     &XV(600)
      DOUBLE PRECISION XT,XTX,DETA,XV,X,Y,W
      CALL DGMTRA (X,XT,N,NN)
```

```
      IJ=0
      DO 31 I=1,N
      DO 32 J=1,NN
      IJ=IJ+1
      XT(IJ)=XT(IJ)*W(I)
   32 CONTINUE
   31 CONTINUE
      CALL DGMPRD(XT,Y,DETA,NN,N,1)
      CALL DGMPRD (XT,X,XTX,NN,N,NN)
      CALL DGELG(DETA,XTX,NN,1,.1E-15,IER)
      IF (IER.NE.0) WRITE(6,15) IER
      DO 4 IS=1,NN
      BETA(IS)=SNGL(DETA(IS))
    4 CONTINUE
      RETURN
   15 FORMAT('  JOB BOMBED IER=',I2)
      END
C                                                                       GMTR  10
C     ..................................................................GMTR  20
C                                                                       GMTR  30
C        SUBROUTINE DGMTRA                                              GMTR40
C                                                                       GMTR  50
C        PURPOSE                                                        GMTR  60
C           TRANSPOSE A GENERAL MATRIX                                  GMTR  70
C                                                                       GMTR  80
C        USAGE                                                          GMTR  90
C           CALL DGMTRA(A,R,N,M)                                        GMTR 100
C                                                                       GMTR 110
C        DESCRIPTION OF PARAMETERS                                      GMTR 120
C           A - NAME OF MATRIX TO BE TRANSPOSED                         GMTR 130
C           R - NAME OF RESULTANT MATRIX                                GMTR 140
C           N - NUMBER OF ROWS OF A AND COLUMNS OF R                    GMTR 150
C           M - NUMBER OF COLUMNS OF A AND ROWS OF R                    GMTR 160
C                                                                       GMTR 170
C        REMARKS                                                        GMTR 180
```

```
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A         GMTR 190
C           MATRICES A AND R MUST BE STORED AS GENERAL MATRICES         GMTR 200
C                                                                       GMTR 210
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  GMTR 220
C           NONE                                                        GMTR 230
C                                                                       GMTR 240
C        METHOD                                                         GMTR 250
C           TRANSPOSE N BY M MATRIX A TO FORM M BY N MATRIX R           GMTR 260
C                                                                       GMTR 270
C     ••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••GMTR 280
C                                                                       GMTR 290
      SUBROUTINE DGMTRA(A,R,N,M)                                        GMTR 300
      REAL*8 A(1),R(1)                                                  GMTR 310
C                                                                       GMTR 320
      IR=0                                                              GMTR 330
      DO 10 I=1,N                                                       GMTR 340
      IJ=I-N                                                            GMTR 350
      DO 10 J=1,M                                                       GMTR 360
      IJ=IJ+N                                                           GMTR 370
      IR=IR+1                                                           GMTR 380
   10 R(IR)=A(IJ)                                                       GMTR 390
      RETURN                                                            GMTR 400
      END                                                               GMTR 410
C                                                                       GMPR  10
C     ••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••GMPR  20
C                                                                       GMPR  30
C        SUBROUTINE DGMPRD
C                                                                       GMPR  50
C        PURPOSE                                                        GMPR  60
C           MULTIPLY TWO GENERAL MATRICES TO FORM A RESULTANT GENERAL   GMPR  70
C           MATRIX                                                      GMPR  80
C                                                                       GMPR  90
C        USAGE                                                          GMPR 100
C                                                                       GMPR 120
C        DESCRIPTION OF PARAMETERS                                      GMPR 130
```

```
C           A - NAME OF FIRST INPUT MATRIX                              GMPR 140
C           B - NAME OF SECOND INPUT MATRIX                             GMPR 150
C           R - NAME OF OUTPUT MATRIX                                   GMPR 160
C           N - NUMBER OF ROWS IN A                                     GMPR 170
C           M - NUMBER OF COLUMNS IN A AND ROWS IN B                    GMPR 180
C           L - NUMBER OF COLUMNS IN B                                  GMPR 190
C                                                                       GMPR 200
C        REMARKS                                                        GMPR 210
C           ALL MATRICES MUST BE STORED AS GENERAL MATRICES             GMPR 220
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A         GMPR 230
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX B         GMPR 240
C           NUMBER OF COLUMNS OF MATRIX A MUST BE EQUAL TO NUMBER OF ROWGMPR 250
C           OF MATRIX B                                                 GMPR 260
C                                                                       GMPR 270
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  GMPR 280
C           NONE                                                        GMPR 290
C                                                                       GMPR 300
C        METHOD                                                         GMPR 310
C           THE M BY L MATRIX B IS PREMULTIPLIED BY THE N BY M MATRIX A GMPR 320
C           AND THE RESULT IS STORED IN THE N BY L MATRIX R.            GMPR 330
C                                                                       GMPR 340
C     ..................................................................GMPR 350
C                                                                       GMPR 360
      SUBROUTINE DGMPRD(A,B,R,N,M,L)                                    GMPR 370
      REAL*8 A(1),B(1),R(1)                                             GMPR 380
C                                                                       GMPR 390
      IR=0                                                              GMPR 400
      IK=-M                                                             GMPR 410
      DO 10 K=1,L                                                       GMPR 420
      IK=IK+M                                                           GMPR 430
      DO 10 J=1,N                                                       GMPR 440
      IR=IR+1                                                           GMPR 450
      JI=J-N                                                            GMPR 460
      IB=IK                                                             GMPR 470
      R(IR)=0                                                           GMPR 480
```

```
      DO 10 I=1,M                                                       GMPR 490
      JI=JI+N                                                           GMPR 500
      IB=IB+1                                                           GMPR 510
   10 R(IR)=R(IR)+A(JI)*B(IB)                                           GMPR 520
      RETURN                                                            GMPR 530
      END                                                               GMPR 540
```

XIII. APPENDIX D: COMPUTER PROGRAM EXTN

```
C  PROGRAM  EXTN  -  SIMULATED EXTRACTION DATA
      REAL INHA,INA
      DOUBLE PRECISION A
      READ(5,1)D,P
      WRITE(6,100)
  100 FORMAT('1',T6,'A',T20,'HA',T31,'HAO',T43,'HDADO',T59,'H',
     &T70,'INHA',T83,'INA'/)
  250 READ(5,2,END=300)VOL,INHA,INA
    1 FORMAT(2F10.5)
    2 FORMAT(3E10.4)
      BETA=6.09E03
      ERR=1.0E-5
      A=INA
      AFAC=100.
   10 AINC=INHA/AFAC
   20 A=A+AINC
      H=A-INA
      HA=BETA*A*H/VOL
      HAO=P*HA
      HDADO=(D/VOL)*(P*HA)**2
      TEST=HAO+2*HDADO+HA+A-INA-INHA
      IF(ABS(TEST).LE.ERR) GO TO 70
      IF(TEST.LT.0.0) GO TO 20
      A=A-AINC
      AFAC=AFAC*10.
      GO TO 10
   70 CONTINUE
      A=A/VOL
      HA=HA/VOL
      HAO=HAO/VOL
      HDADO=HDADO/VOL
      H=H/VOL
      WRITE(6,101)A,HA,HAO,HDADO,H,INHA,INA
  101 FORMAT(E12.6,6(3X,E10.4))
      GO TO 250
  300 STOP
      END
```

XIV. APPENDIX E: EXTN PROGRAM FOR SR-52

LOC	CODE	KEY	LOC	CODE	KEY
0	43	LBL		55	÷
	11	A		43	RCL
	36	IND		00	0
	42	STO		05	5
	00	0	50	54	)
5	00	0		12	B
	01	1		46	LBL
	44	SUM		12	B
	00	0		53	(
	00	0	55	42	STO
10	81	HLT		01	1
	46	LBL		00	0
	16	A'		85	+
	53	(		53	(
	43	RCL	60	53	(
15	00	0		42	STO
	08	8		65	×
	85	+		43	RCL
	53	(		00	0
	43	RCL	65	02	2
20	00	0		54	)
	06	6		85	+
	55	÷		53	(
	43	RCL		42	STO
	00	0	70	40	X^2
25	09	9		65	×
	54	)		02	2
	54	)		65	×
	53	(		43	RCL
	53	(	75	00	0
30	42	STO		01	1
	00	0		55	÷
	08	8		43	RCL
	65	×		00	0
	53	(	80	05	5
35	42	STO		54	)
	75	-		85	+
	43	RCL		43	RCL
	00	0		00	0
	07	7	85	08	8
40	54	)		75	-
	54	)		43	RCL
	65	×		00	0
	43	RCL		06	6
	00	0	90	75	-
45	03	3		43	RCL

LOC	CODE	KEY	LOC	CODE	KEY
	00	0		42	STO
	07	7		00	0
	54	)		08	8
95	54	)	140	01	1
	53	(		00	0
	80	ifpos		49	PROD
	85	+		00	0
	50	stflg		09	9
100	00	0	145	16	A'
	94	+/-		46	LBL
	41	GTO		15	E
	01	1		53	(
	01	1		43	RCL
105	02	2	150	01	1
	46	LBL		00	0
	85	+		55	÷
	22	INV		19	D'
	50	stflg		54	)
110	00	0	155	42	STO
	75	-		01	1
	43	RCL		02	2
	00	0		53	(
	04	4		43	RCL
115	54	)	160	00	0
	94	+/-		08	8
	80	ifpos		55	÷
	15	E		19	D'
	60	ifflg		54	)
120	00	0	165	42	STO
	16	A'		01	1
	53	(		01	1
	43	RCL		53	(
	00	0		53	(
125	08	8	170	43	RCL
	75	-		00	0
	53	(		08	8
	43	RCL		75	-
	00	0		43	RCL
130	06	6	175	00	0
	55	÷		07	7
	43	RCL		54	)
	00	0		55	÷
	09	9		19	D'
135	54	)	180	54	)
	54	)		28	LOG

LOC	CODE	KEY
	94	+/-
	42	STO
	01	1
185	05	5
	53	(
	43	RCL
	01	1
	02	2
190	65	×
	43	RCL
	00	0
	02	2
	54	)
195	42	STO
	01	1
	03	3
	53	(
	42	STO
200	40	X^2
	65	×
	43	RCL
	00	0
	01	1
205	54	)
	42	STO
	01	1
	04	4
	43	RCL
210	01	1
	05	5
	81	HLT
	46	LBL
	19	D'
215	43	RCL
	00	0
	05	5
218	56	rtn