

DISTRIBUTION OF LANTHANUM  
BETWEEN AQUEOUS THIOCYANATE  
AND ISOPHORONE

by

CHESTER RONALD BEAM

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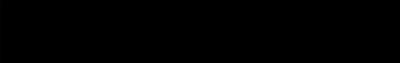
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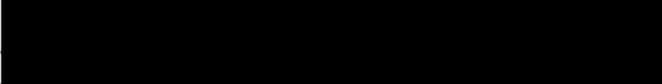
June 1956

APPROVED:

  
Associate Professor of Chemistry  
In Charge of Major

  
Chairman of Department of Chemistry

  
Chairman of School Graduate Committee

  
Dean of Graduate School

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# DISTRIBUTION OF LANTHANUM BETWEEN AQUEOUS THIOCYANATE AND ISOPHORONE

## INTRODUCTION

The separation of the lanthanide elements has occupied the minds of chemists for over one hundred and fifty years. The lanthanides consist of elements 57 through 71. Lanthanum and lutecium, elements 57 and 71, are not inner transition elements since lanthanum has no 4f electrons and lutecium has a full shell of fourteen.<sup>1</sup> The only difference in electronic structure in the lanthanide series is in the 4f electron shell, which accounts for the similarity in the chemical properties of the series. The most stable valence of all of the elements in this series is plus three, although cerium, terbium, and praseodymium also exhibit valencies of plus four and europium, samarium and ytterbium exhibit plus two valencies; however, tetravalent cerium and divalent europium are the only non-trivalent ions which are stable in aqueous solution.

The addition of electrons into the deeply buried 4f quantum shell attendant with the increase in nuclear charge gives rise to a contraction in atomic volume from lanthanum to lutecium. This "lanthanide contraction" is exhibited as a steady decrease in the radii of the trivalent ions. Such differences in properties as exist among the members of this series in a given oxidation state may be

<sup>1</sup> Lanthanum  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^1 6s^2$   
Lutecium  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^1 6s^2$

ascribed to size differences resulting from this contraction. The contraction is sufficient among the lanthanides that atomic and ionic radii drop below the corresponding values for yttrium, element 39. The values for yttrium correspond roughly to those of holmium and dysprosium, making separation of these three elements exceedingly difficult.

It has only been since about 1940 that a satisfactory method of separation for pound quantities of the individual lanthanides has been developed. Up to about 1940, the lanthanides, with the exception of cerium, were almost always separated by fractional precipitation by a variety of anions. (22, pp. 260-265) (25, pp. 51-69) (6, p. 348) Prior to 1939, cerium was separated by exploiting its dual valency. By oxidation of strongly basic, trivalent cerium to the feebly basic, quadrivalent state, almost selective precipitation of cerium was obtained.

That praseodymium and terbium formed both tri and quadrivalent oxides had been known for many years, but not until 1939 was it found that terbium could be oxidized in hydroxide melts, either electrolytically or by potassium chlorate. (3, pp. 536-537) Trivalent hydrated lanthanide oxides are quite soluble in fused  $\text{KOH}\cdot\text{H}_2\text{O}$  at 300-320°C, but oxidation of  $\text{Pr}_2\text{O}_3$  and  $\text{Tb}_2\text{O}_3$  to the quadrivalent state renders them non-competitors for the limited amount of water in the system. They therefore precipitate as the temperature increases

above that at which water is retained. (13, pp. 15-20) These higher oxides can be reclaimed by decantation of the melt and are not easily attacked by acetic acid. By using these two procedures, their separation is quite easily accomplished.

Early studies on the bivalent states of samarium, europium and ytterbium showed a close resemblance existed between these and the alkaline earths. It was found that by treating a solution containing the trivalent lanthanide acetates with sodium amalgam that samarium, europium and ytterbium were reduced to the divalent state and extracted into the amalgam. This led to a rather simple method of separating these elements from the nondivalent lanthanides. (14, pp. 398-401)

When a lanthanide chloride mixture is heated with calcium metal, the resulting "mishmetal" contains none of the potentially divalent lanthanides. Samarium, europium and ytterbium are reduced to the divalent state and are recovered in the calcium chloride slag. This method shows great promise for large scale separation. (18, pp. 15-20)

The use of ion exchange in lanthanide separations was highly developed by the Manhattan Project workers. (20, pp. 2769-2777) In the lanthanide series, the adsorption sequence is La, Ce, Pr, Nd, Sm, Eu, etc., but in the presence of citric acid this sequence is reversed. A technique was then developed, based on elution of adsorbed ions from columns of ion exchange materials, with solutions

which form complexes with the adsorbed ions. (9, pp. 1200-1201)

One disadvantage of ion exchange systems is that separations by this means are confined to relatively small quantities of oxides. Moreover, in spite of the ease of operating ion-exchange columns, they are relatively inefficient.

In an effort to enhance the solubility differences for fractional precipitation schemes, it was found that sequestering agents, such as nitrilo-triacetic acid, ethylene diamine tetra-acetic acid and natural amino acids, would sequester the lanthanides in basic solutions and that these sequestered compounds were reprecipitated on reacidifying. (8, pp. 784-787) This method depended upon the pH values at which the various lanthanide complexes were stable.

There have been numerous papers published in the literature concerning the possibility of separating the lanthanides by solvent-extraction processes. A concept much used in solvent-extraction, but applicable to any separation process, is the separation factor. (23, pp. 474-475) The separation factor between two metals (A,B),

is defined as 
$$\frac{A \text{ (phase 1)}}{B \text{ (phase 1)}} \bigg/ \frac{A \text{ (phase 2)}}{B \text{ (phase 2)}}$$

This ratio is always expressed as a number equal to or greater than 1. It provides a convenient means of comparing systems and is independent of concentrations.

Peppard, Farris, Gray and Mason (17, pp. 294-301) have investigated the equilibrium distribution ratios of various lanthanide nitrates between an organic phase of tributyl ortho phosphate, with

and without diluents, and aqueous nitric acid solutions. They found that while the separation factors were about one when dilute nitric acid was used, the separation factors became more favorable with increasing acid concentrations and using this method plus dilute lanthanide solutions they succeeded in separating the lanthanides into two groups.

Weaver, Tepp and Kappelman (24, pp. 474-475) improved upon the procedure of Peppard, et. al., and succeeded in producing one kilogram of 95% gadolinium oxide with the remaining 5% consisting of samarium and yttrium oxides. They started with a 20-30% gadolinium fraction, used numerous batch extractions, and subsequently extracted it repeatedly in York Scheibel columns. At all times they maintained high nitric acid concentrations, above 10 normal, and permitted the lanthanide concentrations to diminish in each subsequent extraction.

Bechinski, Smute and Spedding (4, pp. 2-29) continued this work with TBP, using undiluted TBP and aqueous lanthanide nitrates without using nitric acid or salting out agents. Separation factors increase with increasing lanthanide concentration and are almost independent of the composition of the lanthanide nitrate mixture. They found that by keeping the concentration of the lanthanides high in the extractor and by recycling the product streams, it is possible to make very significant separations in only a few stages.

Templeten and Petersen (19, p. 3967) carried out batch extractions of aqueous lanthanum and neodymium nitrate mixtures with

n-hexyl alcohol. The aqueous phase was kept about 90% saturated in total nitrates. Two single extractions showed separation factors of 1.48 and 1.55. A three stage fractionation was also performed with an overall separation factor of 2.14 for three stages and an average of 1.29 for each stage.

In 1941, Appleten and Selwood (1, p. 2029) reported on the solubilities of neodymium chloride, iodide, nitrate, thiocyanate, glycolate, acetate, citrate and acetylacetonate in a wide variety of hydrocarbons, ethers, alcohols, ketenes and esters. Neodymium thiocyanate is very soluble in butyl alcohol and although this solvent is appreciably soluble in water, it appeared to offer the best hope of success. An aqueous solution of lanthanum and neodymium thiocyanates was thoroughly shaken with an equal volume of n-butyl alcohol. The mass transfer was about 50% and the separation factor was 1.06.

Little reference was made in the work on liquid extraction to the actual molecular species involved in the transfer of the lanthanide elements from an aqueous phase to an organic phase. The purpose of this work is to gain some knowledge of the ionic species involved in the transfer of the lanthanide elements from an aqueous thiocyanate phase to an organic phase.

## PRELIMINARY EXPERIMENTS

An early routine study of different alcohols, ketenes, esters and other organic solvents was made to gain some insight into the nature of the organic groups necessary to extract lanthanum thiocyanate. It was found that lower alcohols, dissolved in higher alcohols and ketenes, when equilibrated with aqueous lanthanum thiocyanate, formed two phase systems with the lanthanum distributed between the two phases. Because of large phase volume changes this type of system was not considered feasible for continuous extraction. However, isophorone (1, 5, 5, trimethylcyclohexenone-3), cyclohexanone and cyclohexanol were observed to exhibit the same properties without the addition of the lower alcohol. Isophorone was chosen for further study because it showed the lowest volume change on equilibration with aqueous thiocyanate solution.

Table 1 shows the conditions necessary for lanthanum to distribute between an aqueous phase and an organic phase. These data indicate that both thiocyanate and a cyclic ketone or alcohol are necessary for the lanthanum to distribute. While the distribution factor for lanthanum is much higher when cyclohexanone is used as the organic layer, the miscibility at high thiocyanate concentrations is a marked disadvantage in its use.

TABLE 1

## CONDITIONS FOR LANTHANUM DISTRIBUTION BETWEEN TWO PHASES

<u>Initial Aqueous Conditions</u>			<u>Initial Organic Conditions</u>		<u>Conditions After Equilibrating</u>		
La(NO <sub>3</sub> ) <sub>3</sub> Molarity	NH <sub>4</sub> CNS Molarity	Aqueous Volume	Organic Solvent	Organic Volume	Aqueous Volume	Organic Volume	Distribution Factor
0.554	0.944	50	Isophorone	50	47.1	52.4	0.0842
0.554	0.944	50	Cyclohexanone	50	41.9	57.3	0.125
0.554	0.944	50	Cyclohexanone	50	50.0	48.8	0.260
—	1.89	50	Cyclohexanone	50	miscible		
—	1.89	50	Isophorone	50	47.1	53.3	—
0.554	0.944	50	Methyl Isobutyl ketone	50	49.9	50.0	nil

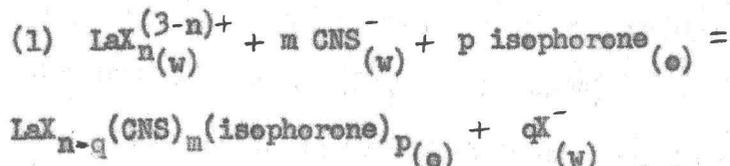
## THEORETICAL CONSIDERATIONS

Lanthanum was chosen for this work because of its availability, inexpensiveness, and single valency of plus three in aqueous solution. (11, pp. 286-295)

It may be assumed that lanthanum, in aqueous solution, is an ion of the form  $\text{LaX}_n(3-n)^+$ , where X in this case is a monovalent anion, and n is a small interger or zero. In a solution consisting of lanthanum nitrate and ammonium thiocyanate, the nature of X can be limited to thiocyanate, nitrate or hydroxide.

The principles of solvent extraction have recently been outlined by Martell and Calvin. (15 pp. 451-468) The method depends on the formation of nonionized complex compounds and their slight solubility in water as compared to their solubility in water immiscible organic solvents. In the system ammonium thiocyanate-lanthanum nitrate-isophorone, there is apparently no chelation taking place. The structure for isophorone as shown in Appendix A doesn't show any obvious tendency for ring formation as a chelating agent. The rather low distribution factor would lead one to expect that probably an unionized salt is actually being extracted and therefore, the conditions which would enhance the extraction would be the same as these which would decrease the ionization of the lanthanum salt. The fact that lanthanum is extracted by only a few organic solvents and not by others indicates that some sort of bonding is involved between the lanthanum salt and the isophorone.

The overall equilibrium involved in the transfer of lanthanum between the water phase and the organic phase may be represented by the following equation:



where  $X^{-}$  is either  $\text{CNS}^{-}$ ,  $\text{NO}_3^{-}$  or  $\text{OH}^{-}$  and (o) refers to the organic phase and (w) refers to the aqueous phase. We may now define an equilibrium constant as:

$$(2) K = \frac{[\text{LaX}_{n-o}(\text{CNS})_m(\text{isophorene})_p] [\text{X}]^q}{[\text{LaX}_n^{(3-n)}] [\text{CNS}]^m [\text{isophorene}]^p}$$

Defining a distribution factor D as:

$$(3) D = \frac{[\text{LaX}_{n-o}(\text{CNS})_m(\text{isophorene})_p]}{[\text{LaX}_n^{(3-n)}]}$$

We may now write:

$$(4) K = \frac{D [\text{X}]^q}{[\text{CNS}]^m [\text{isophorene}]^p}$$

In order to use the above equations, it is necessary to make the further assumption that the activity coefficients are constant in the range of concentrations used. This will not give a true value for K, but it will not affect the values of m and p appreciably, while the errors associated with this assumption will be partially alleviated by the use of logarithmic plots.

Taking logarithms of both sides of equation (4) and rearranging:

$$(5) \log D = m \log \text{CNS} + p \log \text{isophorene} - q \log X + \log K$$

This is the form of the equation which will be used in determining  $m$ ,  $p$ , and  $q$ .

DETERMINATION OF  $q$  AND THE NATURE OF  $X$ 

As stated before under theoretical considerations,  $X$  can be limited to thiocyanate, hydroxide or nitrate. Equation (5) will be used for this purpose.

$$(5) \log D = m \log \text{CNS} + p \log \text{isopherone} - q \log X + \log K$$

Rewritten in the form:

$$(6) \log D = -q \log X + \log K^I$$

where  $\log K^I = m \log \text{CNS} + p \log \text{isopherone} + \log K$

this equation forms a basis of a method for determining the dependence of  $D$  on hydroxide or nitrate when the rest of the system is held essentially constant. It will give no information on thiocyanate because of the CNS factor in the  $\log K^I$  term.

Table II shows the dependence of the distribution factor on the nitrate concentration. The total initial aqueous volume was fifty milliliters in all cases and was 0.508 molar in lanthanum nitrate and 1.42 molar in ammonium thiocyanate. The ammonium nitrate solution was made up from reagent grade ammonium nitrate dissolved in distilled water. The stock solution of  $\text{NH}_4\text{NO}_3$  was 3.00 molar. Stock solutions of lanthanum nitrate, ammonium thiocyanate and ammonium nitrate were pipetted into a separatory funnel and the volume was diluted to fifty milliliters with distilled water. Fifty milliliters of isopherone was added and the mixture was shaken for fifteen minutes. After shaking, the phases were separated and the volumes noted. The organic layer was back extracted three times

with very dilute nitric acid to remove the lanthanum. The three extractions were combined and the lanthanum precipitated with ammonia and ignited for two hours at 800°C. The lanthanum remaining in the aqueous layer was determined by difference.

TABLE II

VARIATION OF D WITH  $\text{NH}_4\text{NO}_3$  CONCENTRATION

Molarity $\text{NH}_4\text{NO}_3$	Aqueous Volume	Organic Volume	D	log D	log $\text{NH}_4\text{NO}_3$
1.524	46.7	53.0	0.1520	-0.8182	0.1830
1.584	47.0	53.0	0.1516	-0.8193	0.1872
1.644	47.4	53.0	0.1542	-0.8119	0.1914
1.704	47.3	53.2	0.1544	-0.8114	0.1956
1.764	47.0	53.2	0.1523	-0.8173	0.1998
1.824	46.8	53.5	0.1502	-0.8233	0.2038

## Initial conditions

Aqueous volume	50 ml.
Organic volume	50 ml.

Graph I shows a plot of log D vs log  $\text{NO}_3$  and has a slope of -0.02. This reveals that q in this reaction is essentially zero. The nitrate ion is either not directly involved in the reaction or is not exchanged in forming the organic soluble complex.

The same procedure is used in determining the dependence of the distribution factor on the hydroxide concentration. In this case, it is impractical to add hydroxide because of the formation of insoluble lanthanum hydroxide and dilute nitric acid was added instead. Equation (6) in the form:

$$(6) \log D = -q \log \frac{10^{-14}}{H^+} + \log K^I$$

was rearranged to

$$(7) \log D = q \log H + \log K^{II}$$

where  $K^{II}$  includes the  $10^{-14}$  factor. Using equation (7) and nitric acid, the dependence of the distribution factor on hydroxide was determined.

Table III shows the results of varying the nitric acid concentration while holding the other variables essentially constant. The 0.628 molar nitric acid stock solution was made up by diluting reagent grade nitric acid with distilled water. The other reagents and procedure was the same as above for the determination of the dependence of distribution factor on the ammonium nitrate concentration.

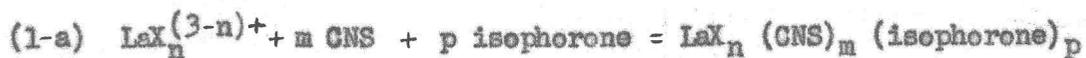
TABLE III

VARIATION OF D WITH  $HNO_3$  CONCENTRATION

Molarity $HNO_3$	Aqueous Volume	Organic Volume	D	log D	log $HNO_3$
0.00000	46.5	53.0	0.1943	-0.721	-----
0.00134	46.8	53.6	0.1790	-0.747	-2.872
0.00262	47.9	52.4	0.1797	-0.746	-2.582
0.00379	49.7	53.3	0.1875	-0.727	-2.422
0.00497	50.5	52.9	0.1942	-0.712	-2.304
0.00607	51.7	53.3	0.1888	-0.724	-2.217
Initial conditions					
Aqueous volume		50 ml.			
Organic volume		50 ml.			

Graph II shows a plot of  $\log D$  vs  $\log \text{HNO}_3$  and has a slope of 0.05. This reveals that the hydroxide ion is not directly involved in the reaction or is not exchanged in forming the organic soluble complex.

Using the above results equation (1) may be rewritten



and using the same reasoning as before equation (4) may be rewritten

$$(4-a) \quad K = \frac{D}{(\text{CNS})^m (\text{isophorone})^p}$$

These two equations will be used in determining the variation of distribution factor on the isophorone and thiocyanate concentrations.

Equation (4-a) will also be used in determining the nature of  $X^-$ .

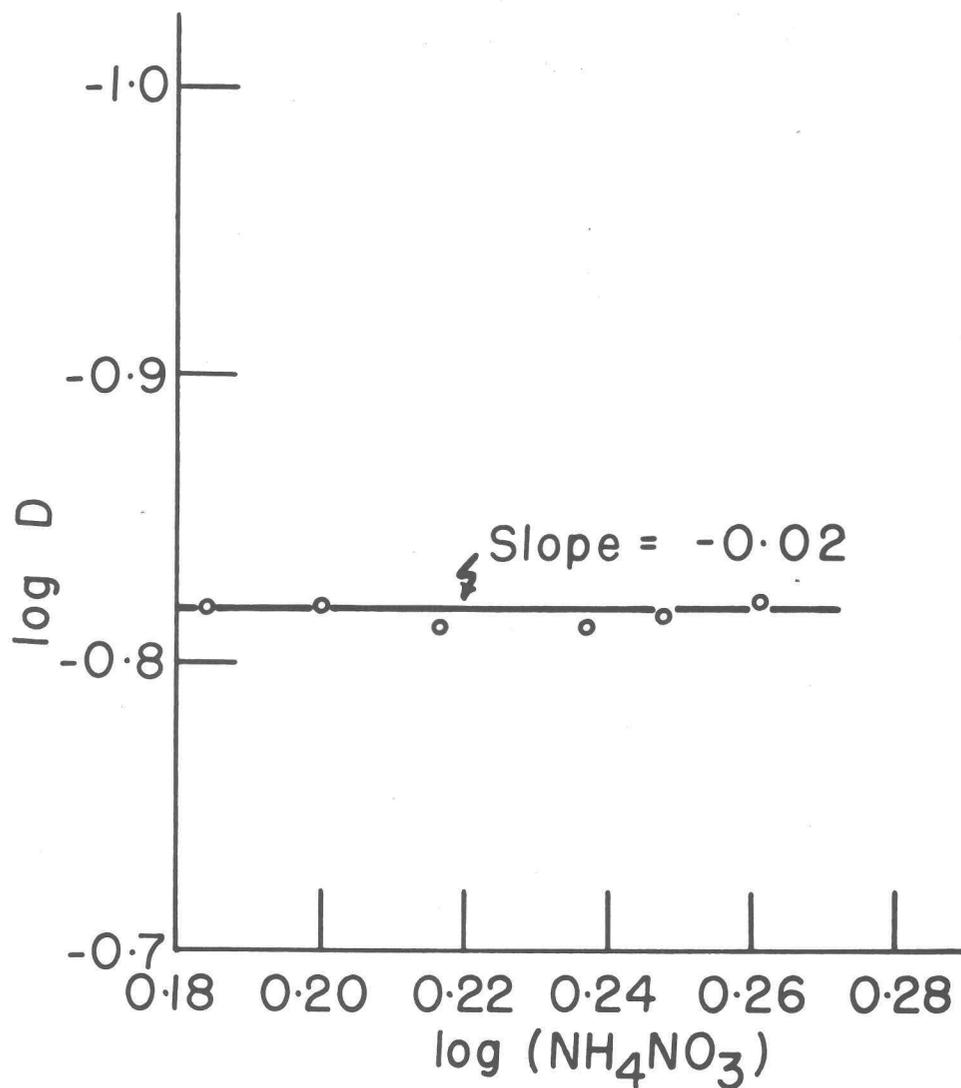


Figure 1. -  $\log D$  vs  $\log(\text{NH}_4\text{NO}_3)$

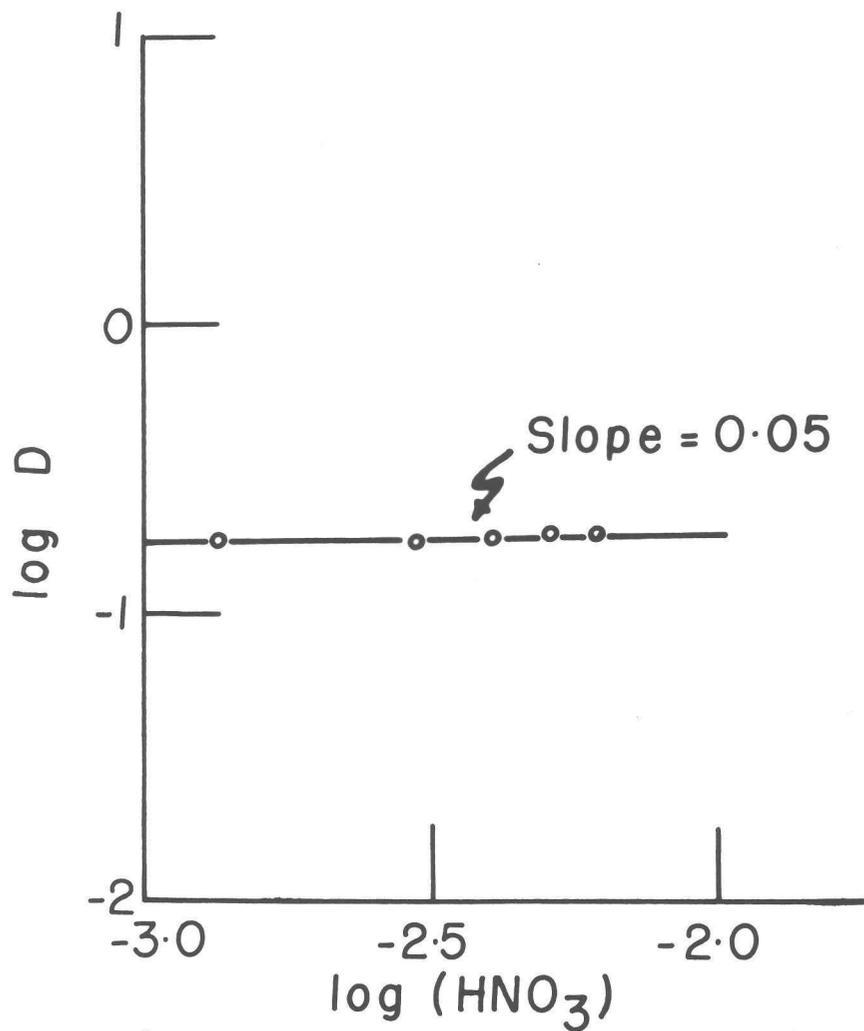


Figure 2. -  $\log D$  vs  $\log (\text{HNO}_3)$

## DEPENDENCE OF DISTRIBUTION FACTOR ON THE ISOPHORONE CONCENTRATION

In the preliminary work on this system it was observed that no transfer of lanthanum took place when methyl isobutyl ketone (MIBK) was used as the water immiscible phase. This presumably is because the MIBK will not combine chemically with the aqueous lanthanum complex. Mixtures of MIBK and isophorone do extract the lanthanum complex, however, so it may be assumed that the lanthanum thiocyanate isophorone complex is soluble in MIBK. Isophorone and MIBK are miscible in all proportions and MIBK was used as an inert diluent for the isophorone.

In determining the dependence of the distribution factor on isophorone concentration, equation (4-a) will be used:

$$(4-a) \quad K = \frac{D}{(\text{CNS})^m (\text{isophorone})^p}$$

Taking logarithms and rearranging, equation (8) is obtained.

$$(8) \quad \log D = \log K + m \log \text{CNS} + p \log \text{isophorone}$$

If the thiocyanate concentration is held essentially constant, equation (8) may be simplified to:

$$(9) \quad \log D = p \log \text{isophorone} + \log K^{\text{III}}$$

where  $\log K^{\text{III}}$  includes the  $m \log \text{CNS}$  term.

The isophorone used was reagent grade and the purity was greater than 98%. The results of any minor impurity would show up as a constant factor in equation (4-a) and would then be absorbed in the  $\log K^{\text{III}}$  term in equation (1). Actually, in plotting the results,

the  $\log K^{\text{III}}$  term also included the correction factor for converting milliliters of isophorone in fifty milliliters of organic layer to concentration units.

In the experimental procedure, the initial aqueous layer contained 0.491 molar lanthanum nitrate and 1.56 molar ammonium thiocyanate. Fifty milliliters of aqueous layer was shaken for fifteen minutes with varying amounts of MIBK and isophorone in fifty milliliters of organic layer. There was a volume change on shaking so that the value for milliliters of isophorone was corrected to milliliters of isophorone in fifty milliliters of the organic layer after shaking. After equilibrating, the lanthanum in the organic layer was determined by difference. The distribution factor was determined and corrected for the volume change on mixing.

Table IV shows the dependence of  $D$  on the isophorone concentration in the organic layer. The results of these determinations are plotted in Graph III. The upper portion of the curve indicates that only the complex where  $p = 3$  is important when the organic layer is predominately isophorone. In the lower concentrations, the complexes where  $p = 1$  and  $p = 2$  may possibly be present. It will be noted that when  $\log$  (ml. isophorone) equals 1.699, the organic layer is entirely isophorone and the curve cannot be extended beyond this. Also, in further work with this system, it was found that when undiluted isophorone is used as the organic solvent, the assumption can be made that only the  $p$  equals three complex is present. The presence of the  $p$  equals one and two complexes may be illusory

TABLE IV

## DEPENDENCE OF D ON ISOPHORONE CONCENTRATION

<u>Isophorone</u> <u>ml.</u>	<u>MIBK</u> <u>ml.</u>	<u>Volume after shaking</u>		<u>D</u>	<u>ml. isophorone</u> <u>corrected</u>	<u>log D</u>	<u>log (ml. isophorone)</u>
		<u>Aqueous</u>	<u>Organic</u>				
5	45	50.1	50.1	0.00303	4.99	-2.519	0.6981
10	40	50.0	50.2	0.00504	9.96	-2.298	0.9991
15	35	50.0	50.3	0.0102	14.9	-1.9914	1.1732
20	30	49.9	50.7	0.0167	19.7	-1.777	1.2945
25	25	49.2	50.8	0.0327	24.6	-1.4855	1.3909
30	20	49.6	51.2	0.0580	29.3	-1.237	1.4669
15	35	49.8	50.4	0.00987	14.8	-2.0057	1.1703
20	30	49.7	50.8	0.0158	19.7	-1.8014	1.2945
25	25	49.3	51.0	0.0299	24.5	-1.5244	1.3892
30	20	48.9	51.4	0.0532	29.2	-1.2741	1.4654
35	15	48.1	52.0	0.0834	33.6	-1.0789	1.5263
40	10	47.3	52.9	0.122	37.8	-0.9137	1.5775
45	5	46.4	53.6	0.155	42.0	-0.8097	1.6232

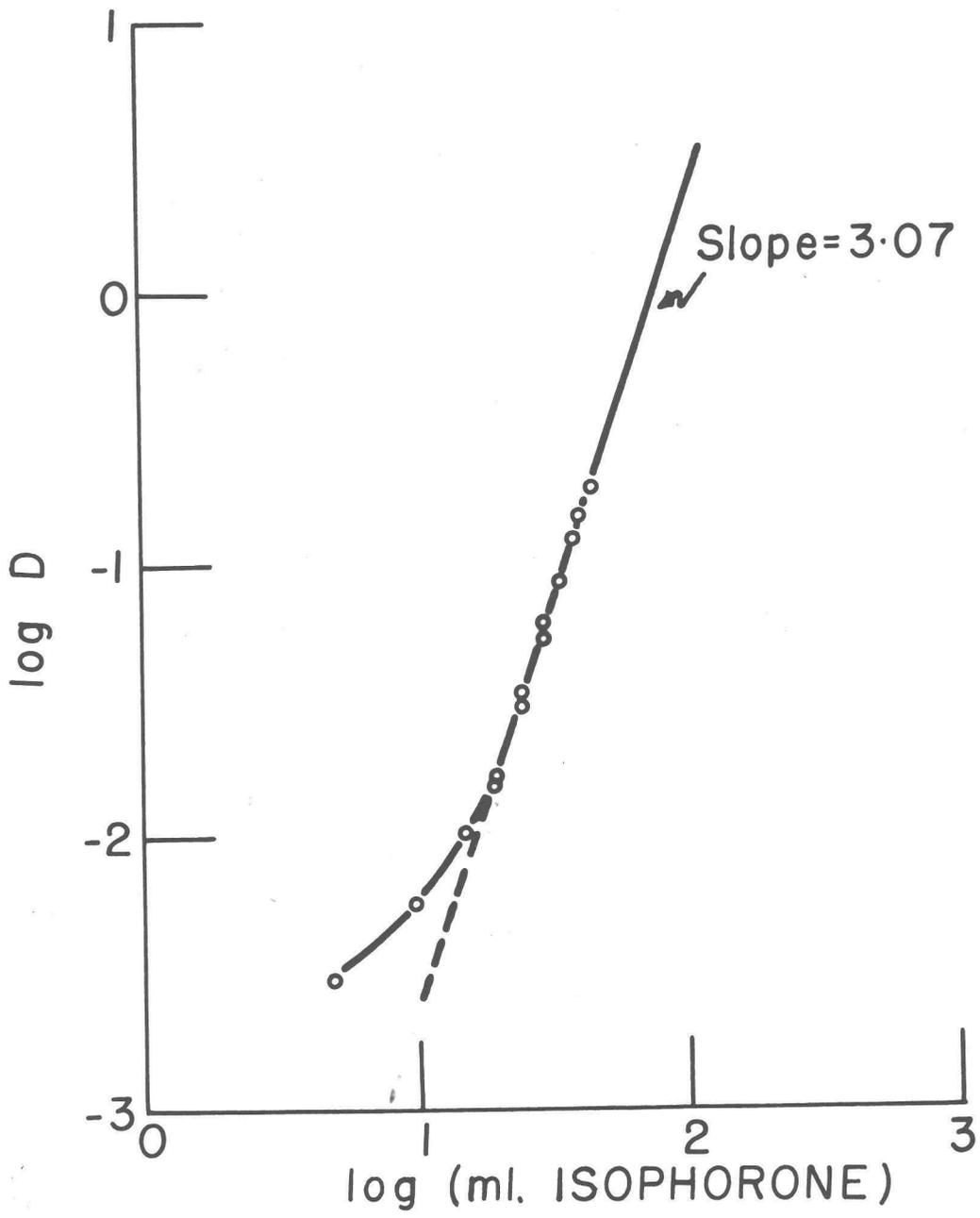
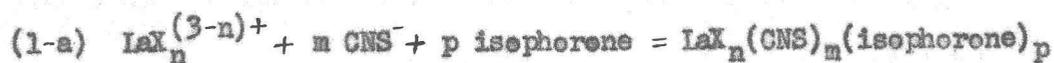


Figure 3. - log D vs log (ml. isophorone)

because small errors in the experimental technique would show up as quite large errors in the distribution factor at these low values.

## DEPENDENCE OF DISTRIBUTION FACTOR ON THIOCYANATE CONCENTRATION

In establishing the dependence of the distribution factor on the thiocyanate concentration it is first necessary to ascertain whether  $X$  is thiocyanate in equation (1-a) and to determine the value of  $n$ .



Using the value of 3 for  $p$  in equation (1-a), equation (4-a) can be written in the following form.

$$(4-b) D = K [\text{isophorene}]^3 [\text{CNS}]^m$$

An examination of equation (4-b) reveals that  $D$  must equal zero when thiocyanate equals zero. A plot of  $D$  vs  $(\text{CNS})^m$  should be a straight line which passes through the origin if the proper values of thiocyanate and  $m$  are used.

A series of determinations were made at 0.495 and 0.248 molar lanthanum and varying amounts of thiocyanate. These results are shown in Table V. In all cases, the initial organic layer was fifty milliliters of isophorene and the value of  $p$  in equation (4-b) was considered as three. The thiocyanate in the aqueous layer was determined by titrating with silver nitrate to a ferric ion end point. The lanthanum was determined as before.

A plot of the results for the determinations at 0.248 molar lanthanum is shown in Figure 4. The distribution factor is plotted against  $(\text{CNS})^m$  for various values of  $m$ . In Figure 4, the value of  $(\text{CNS})$  used was the total aqueous thiocyanate concentration. In all

TABLE V

## DEPENDENCE OF D ON THIOCYANATE CONCENTRATION

## I. Initial Aqueous Lanthanum Molarity 0.495

Phase	Volumes	Aqueous Thiocyanate	D	Aqueous Lanthanum	$[\log D - 3 \log (\text{isophorene})]$	$\log (\text{GNS})$
Aqueous	Organic	Molarity		Molarity		
49.2	51.2	0.258	0.0469	0.478	-3.75	-0.589
48.3	51.9	0.345	0.0681	0.474	-3.57	-0.462
48.0	52.6	0.474	0.121	0.444	-3.28	-0.325
47.2	52.9	0.549	0.150	0.432	-3.17	-0.262
46.1	54.4	0.6944	0.222	0.383	-2.92	-0.160
44.9	55.2	0.769	0.248	0.365	-2.85	-0.115
48.7	51.5	0.218	0.0630	0.473	-3.81	-0.662
47.6	51.8	0.312	0.0889	0.468	-3.54	-0.506
47.1	53.2	0.484	0.156	0.427	-3.23	-0.316
46.2	53.6	0.528	0.206	0.397	-3.08	-0.278
45.6	54.9	0.696	0.271	0.348	-2.90	-0.158
44.2	55.8	0.748	0.319	0.309	-2.78	-0.126

## II. Initial Aqueous Lanthanum Molarity 0.248

48.0	52.0	0.686	0.138	0.223	-3.26	-0.163
47.4	53.1	0.905	0.249	0.201	-2.96	-0.044
46.2	54.4	1.060	0.312	0.192	-2.83	0.025
45.3	55.1	1.300	0.458	0.167	-2.63	0.114
44.0	55.9	1.419	0.537	0.155	-2.52	0.152
42.6	58.0	1.791	0.658	0.147	-2.38	0.254

cases, when the curve is extrapolated to  $D$  equals zero, the curve does not pass through the origin. It should be noted that in this case the extrapolation to  $D$  equals zero does not mean that the curve does not actually pass through the origin but at the concentrations at which the measurements were made that some of the thiocyanate is not available to influence the distribution. This result could only be caused by some of the thiocyanate being complexed in a rather stable manner in the aqueous layer. At the low thiocyanate concentrations in the region of the origin, the complex could be expected to disassociate and the curve pass through the origin.

In Figure 4, the curve for  $m$  equals two is a straight line with the exception of the last point which is displaced on all three curves. This would indicate that the  $\text{La}(\text{CNS})^{\text{II}}$  ion is the predominate specie in the aqueous layer. The  $m$  equal 3 curve exhibits a straight line in the region of high thiocyanate concentration. This would be expected when the total number of thiocyanate ions in the complex is three and the difference between free thiocyanate and total thiocyanate becomes small.

Figure 5 shows the result of assuming the presence of the  $\text{La}(\text{CNS})^{\text{II}}$  ion exclusively in the aqueous phase. In this case the resulting curve does pass through the origin and establishes the presence of the  $\text{La}(\text{CNS})^{\text{II}}$  ion. This result is in agreement with the results of Mattern. (12, pp. 63-65). In solutions of ionic strength of one, lanthanum formed complexes of  $\text{LaCl}^{\text{II}}$  and  $\text{LaNO}_3^{\text{II}}$  in chloride

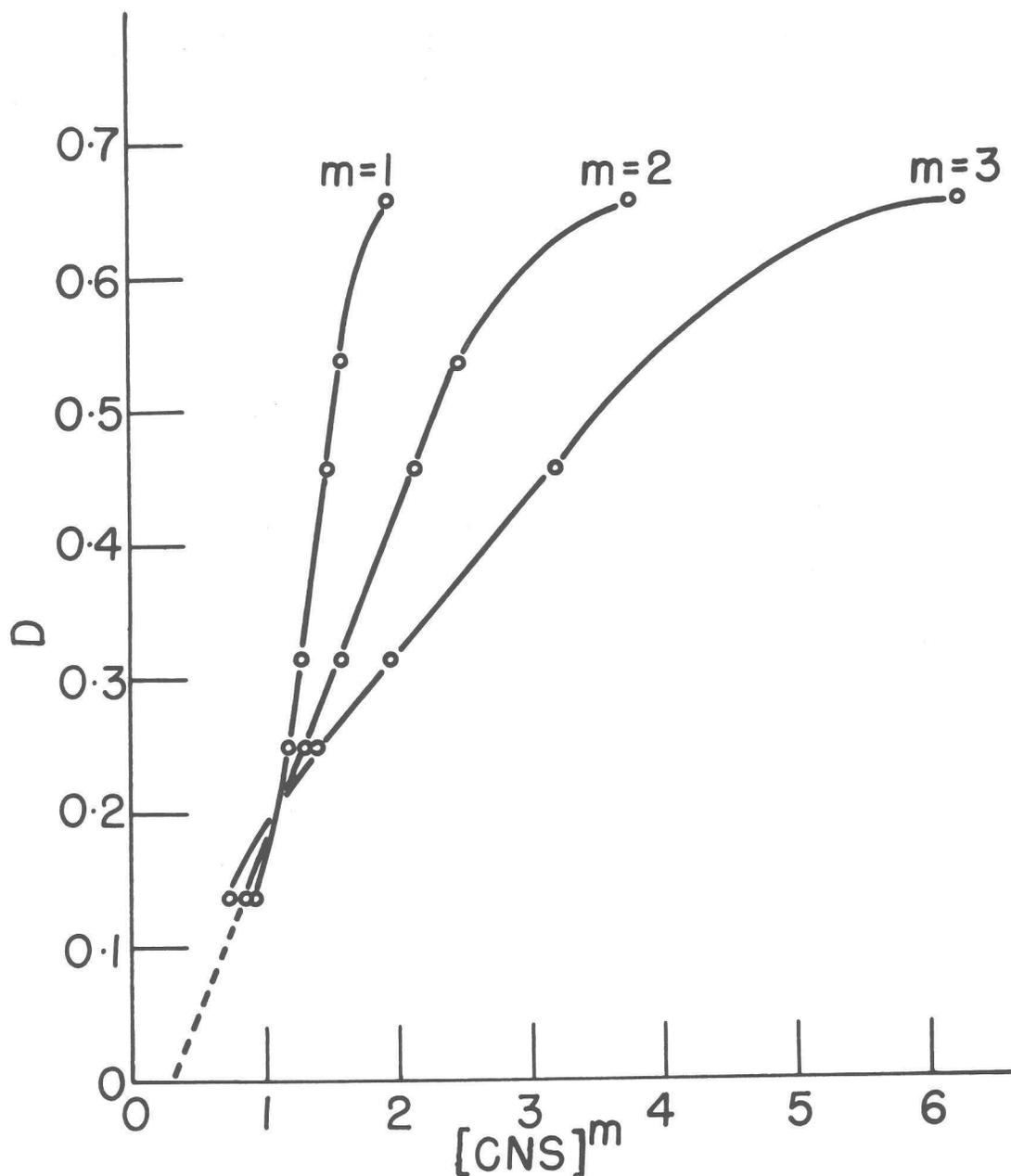


Figure 4.- Variations of  $D$  with thiocyanate concentration raised to the  $m$  power

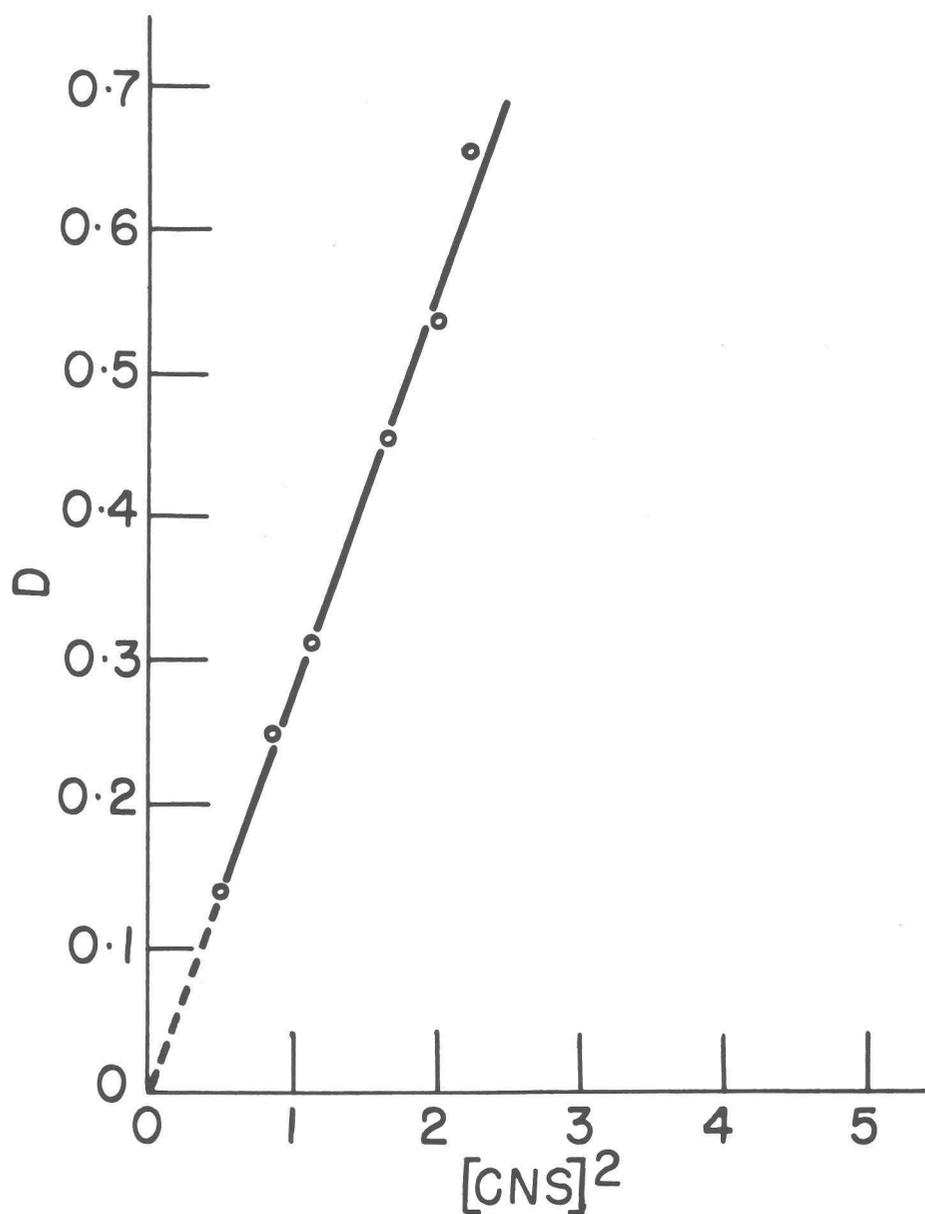


Figure 5.- Variation of D with corrected thiocyanate concentration raised to the second power

and nitrate solutions respectively. Using the stability constants for an ionic strength of one for concentrations which are being used in this study reveals that lanthanum would be from 50-70% associated in chloride solutions as the  $\text{La Cl}^{\ddagger}$  ion. The presence of the bulk of the lanthanum as  $\text{La (CNS)}^{\ddagger}$  in thiocyanate solutions of these concentrations can be reasonably expected.

Using this information and equation (4-b), the true value of  $m$  in equation (1-a) can be determined. Taking logarithms of equation (4-b) and rearranging, equation (10) is obtained and will be used to determine the value of  $m$ .

$$(10) \quad \log D - 3 \log \text{isopherone} = m \log \text{CNS} + \log K$$

In equation (10) the value of thiocyanate used must be the free aqueous thiocyanate concentration. The molarity of the free isopherone in the organic layer is decreased by a significant amount both by the lanthanum present and by dilution on equilibrating. This effect can be calculated and the correction included. Figure 6 shows a plot of  $[\log D - 3 \log (\text{isopherone})]$  vs  $\log \text{CNS}$ . The value of thiocyanate used here is the total aqueous thiocyanate minus the aqueous lanthanum concentration. This amounts to assuming that all of the lanthanum is present as  $\text{La (CNS)}^{\ddagger}$ . The slope of the curve for 0.495 molar lanthanum is 1.90. While the experimental points show some variation, the deviation in the slope from two may be due to the fact that assuming that all of the lanthanum present is in the form of the  $\text{La (CNS)}^{\ddagger}$  ion is not entirely correct. The value of the slope for the 0.248 molar

lanthanum is probably due to the fact that much higher free thiocyanate concentrations are being used and the error associated with the assumption of the  $\text{La}(\text{CNS})^{\text{H}}$  ion is minimized. It is apparent from this work that most but not all of the lanthanum is present in the aqueous layer as the  $\text{La}(\text{CNS})^{\text{H}}$  ion. The proportion of  $\text{La}(\text{CNS})^{\text{H}}$  present in the 0.248 molar lanthanum solutions used here is probably very high. Equation (1-a) may now be written in the final form.



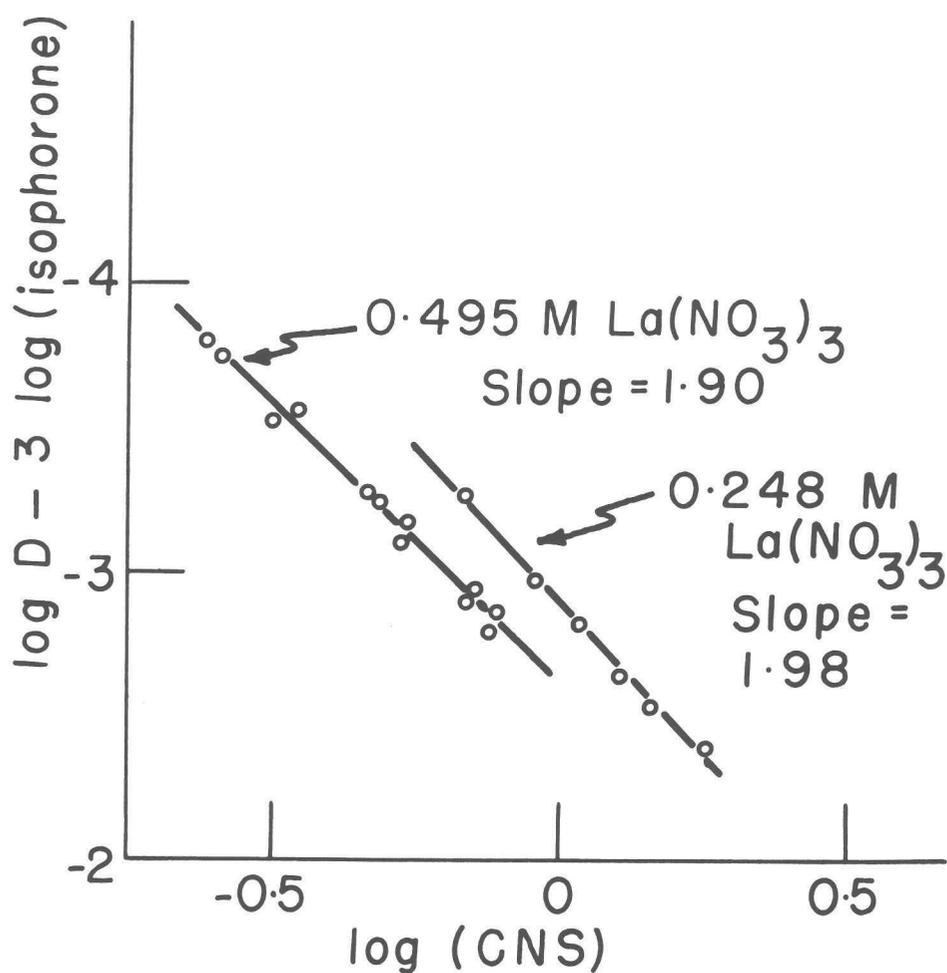


Figure 6.- log D - 3 log (isophorone)  
vs log (CNS)

## DISCUSSION

The results of this investigation show that lanthanum transfers from an aqueous thiocyanate phase to an organic isophorone phase in accordance with the following equation.



In the determination of the dependence of D on the isophorone concentration, the assumption was made that the thiocyanate concentration remained essentially constant. After determining the values of m and n in equation (1-a), a recalculation was made of the dependence of D on the isophorone concentration including the corrections for the change in thiocyanate concentration. The value of p in equation (1-a) was 3.07 when the constancy of the thiocyanate concentration was assumed and 2.94 when the corrections for changing thiocyanate concentrations were included in the calculation. Both of these values vary from three by about two percent and confirm the validity of the initial assumption.

The formula  $\text{La (CNS)}_3 (\text{isophorone})_3$  satisfies the ionic valency of plus three for lanthanum and also satisfies the coordination valency of six for lanthanum.

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**APPENDIX**

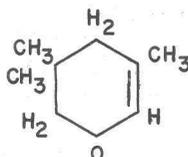
## APPENDIX A

## Reagents Used

Isophorone; 1, 5, 5 trimethylcyclohexenone-3. M. W. 138.20

Eastman Organic Chemicals

Reagent Grade



Cyclohexanol

M. W. 100.16

Reagent Grade

Eastman Organic Chemicals

Cyclohexanone

M. W. 98.14

Reagent Grade

Eastman Organic Chemicals

Lanthanum oxide

Purity 99.97  $\text{La}_2\text{O}_3$

Lindsey Chemical Company, West Chicago, Illinois

Nitric acid

Reagent Grade

Baker and Adamson, Reagent Grade Chemicals

Ammonium Thiocyanate

Reagent Grade

Fisher Scientific Company

## APPENDIX B

## CALCULATION OF VALUES PLOTTED IN GRAPH 6

In plotting Graph 6, equation (10) was used.

$$(10) \quad \log D - 3 \log (\text{isopherone}) = m \log (\text{CNS}) + \log K$$

(a) Calculating  $[\log D - 3 \log (\text{isopherone})]$

The value of isopherone used here was the molarity of the isopherone in the organic layer which was not complexed to the lanthanum.

$$\text{Total isopherone molarity} = \left[ \frac{50 \text{ ml} \times \text{density}}{\text{M. W. isopherone}} \right] \left[ \frac{1000}{\text{organic volume}} \right]$$

$$\text{Organic lanthanum molarity} = \left[ 2 \frac{\text{Wt. La}_2\text{O}_3 \text{ in organic}}{\text{M. W. La}_2\text{O}_3} \right] \left[ \frac{1000}{\text{organic volume}} \right]$$

Total isopherone - 3 (molarity organic lanthanum) =  
molarity of uncomplexed isopherone

$[\log D - 3 \log (\text{isopherone})]$  is then obtained from the above value.  
 $\log D$  is given in table 6.

(b) Calculating  $\log (\text{CNS})$

The value used here was the molarity of uncomplexed aqueous thiocyanate assuming that all of the aqueous lanthanum was in the form  $\text{La} (\text{CNS})^{++}$ .

Total aqueous thiocyanate molarity    aqueous lanthanum molarity  
uncomplexed thiocyanate molarity.

### Sample Calculation

Calculating the first value in Table V is as follows:

(a)  $\log D - 3 \log (\text{isephorone})$

$$\text{Total isephorone molarity} = \left[ \frac{50 \text{ ml} \times .9255 \text{ gm/ml}}{138.2 \text{ gm}} \right] \left[ \frac{1000}{51.2 \text{ ml}} \right] = 6.52$$

$$\text{Organic lanthanum molarity} = \left[ 2 \frac{0.1999}{325.8} \frac{1000}{51.2} \right] = 0.024$$

$$\text{Uncomplexed isephorone} = 6.52 - (3)(0.024) = 6.45 \text{ molar}$$

$$[\log D - 3 \log (\text{isephorone})] = -1.330 - (3)(.809) = -3.75$$

(b)  $\log (\text{CNS})$

$$\text{Total aqueous thiocyanate} = 0.746 \text{ molar}$$

$$\text{Aqueous lanthanum} = 0.478 \text{ molar}$$

$$0.746 - 0.478 = 0.258 \text{ molar uncomplexed thiocyanate}$$

$$\log (\text{CNS}) = 0.589$$