EXTRACTION OF LANTHANUM (III) BY MORIN-METHYL ISOBUTYL KETONE

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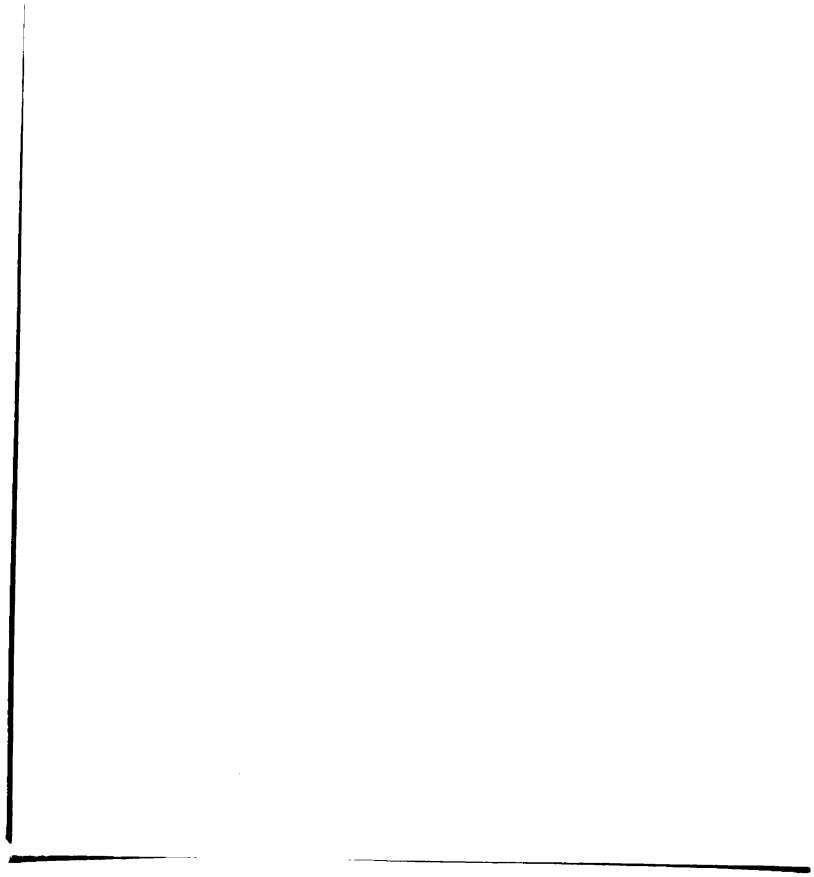

ABSTRACT

EXTRACTION OF LANTHANUM(III) BY MORIN-METHYL ISOBUTYL KETONE

by Yuk-Hang Cheuk

Lanthanum(III) forms with morin a complex which can be extracted quantitatively from an aqueous perchloric acid solution at pH 6.70-6.80 into hexone (methyl isobutyl ketone). Spectrophotometric and spectrofluorometric methods were employed for analyzing the organic phase. The various factors which affect the extraction of this complex in given system were investigated.

The selected volume ratio of organic to aqueous phase was 2 to 1. At pH 6.7-6.8 lanthanum(III) forms a 1:2 complex with morin. It is assumed that the extracted species would be the ion-pair formed between lanthanum(III)-morin and an anion, such as hydroxide, perchlorate, or chloride ion.

The lanthanum(III)-morin complex in hexone is excited by the 365 mμ radiation, and the fluorescence radiation is emitted with peak intensity at 505-510 mμ. Morin hexone solutions do not fluoresce appreciably under these conditions. The absorption band peak of the lanthanum(III)-morin complex and morin are at 410 and 356 mμ respectively.

The absorbance and fluorescence intensities of the complex in hexone vary linearly when the concentration of lanthanum(III) in the aqueous phase is varied between 0-48 γ with 400 γ of morin in hexone. Above 48 γ of lanthanum(III), the absorbance and fluorescence decrease.

When successive extractions were made from an aqueous sample solution, the major part of the lanthanum(III) in the aqueous phase was extracted with the first portion of morin reagent, and up to 28γ of lanthanum(III) can be extracted by this single extraction. The second portion of morin reagent was effective for completing the extraction when the concentration of lanthanum(III) was between 28 to 48γ in the original aqueous sample solution.

The addition of samarium(III) to the original aqueous phase has a slight effect on the fluorescence intensity of the organic phase at very dilute aqueous lanthanum(III) levels.

Lanthanum(III) also can be extracted from aqueous dilute solutions of hydrochloric acid, nitric acid or sulfuric acid into hexone containing 400 γ of morin.

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By

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INTRODUCTION

Liquid - liquid solvent extraction has long been known as a method of separation in analytical procedures. The principles of the distribution (or extraction) method were introduced by Nernst (1891) [22]. He established the constancy of the partition coefficient for species of the same molecular composition distributed between two immiscible solvents, and the possibility of using his distribution law to study the dissociation equilibria of a number of substances in aqueous solution. Shortly afterwards, Hendrixson [11] studied the distribution coefficient between organic and aqueous phases. In recent years, many investigators have shown interest to utilize the extraction technique for separating elements including individual rare earths from ores and sands. A valuable application is in radiochemical separations.

The phenomenon is based upon the fact that if a substance is dissolved in a system of two immiscible or slightly miscible liquids, the substance is distributed between the two layers in a definite manner. The classification of extraction system is based on the type of extractable species formed. Two broad categories are chelate and ion association extraction systems. Most extractable species which involve chelation solely are coordination complexes [18]. The solubility of internal complexes and of a number of complexes of metals with inorganic ligands in organic solvents makes it possible to utilize the distribution method. Furthermore, many of the complexes have a distinct color, enabling them to be adapted to colorimetric or fluorometric analysis.

Many variables are involved to formulate quantitatively the relation between the partition coefficient for a metal in a given system [17], such as the concentrations of the metal ion itself, pH of the aqueous phase,

concentration and type of reagent, temperature, and nature of the organic solvent.

A few organo-lanthanide complexes can be excited in the near ultraviolet and visible region of the spectrum to emit intense fluorescence [10, 14, 23, 35, 38], which is characteristic of the complex. Lanthanum(III), gadolinium(III), and lutetium(III) are the only tripositive lanthanide ions which contain sufficiently stable cation electronic configurations to yield an observable fluorescence.

The work which follows was undertaken to study the distribution of microgram quantities of lanthanum(III) between an aqueous layer and various organic solvents containing the organic reagent morin (2', 4', 3, 5, 7-pentahydroxy flavone).

The interrelationship between absorbance or fluorescence intensity and concentration of lanthanum(III) was to be determined to establish whether or not, extraction followed by measurement of absorbance or fluorescence of the organic phase could form the basis for quantitative determination of small quantities of lanthanum(III) in an original aqueous solution.

HISTORICAL

The book entitled Solvent Extraction in Analytical Chemistry by Morrison and Freiser [20] still represents the only comprehensive treatment of extraction as applied to inorganic analysis. In this book, principles of solvent extraction, apparatus and general technique, extraction systems and separations are discussed thoroughly. More recently, their chapter in Comprehensive Analytical Chemistry [21] has served to present the latest information in a rapidly developing area of analysis. The new edition of Sandell's book [32] Colorimetric Determination of Traces Metals also gives increasing emphasis to extraction methods.

With regards to reviews, a series on extraction written by Craig [3-8] in Analytical Chemistry presents an excellent survey of the developments in the organic and biochemical fields, with emphasis on the technique of countercurrent distribution.

In two review articles by Morrison and Freiser [18, 19], approximately 600 references are cited. The technique as applied to the separation of inorganic and biochemical substances is emphasized.

In a series of articles by Rydberg [25, 26, 27, 28] and other Scandinavian investigators the applicability of the distribution method for the quantitative study of complex formation in solution is demonstrated. To interpret data relating to the extraction of a metal complex by an organic solvent from an aqueous phase of low and constant ionic strength, they also examined the influences of temperature, the metal ion itself and anions in the solution. The possibility of separating metals by extracting some of them as acetylacetonates from aqueous sodium perchlorate solution into the organic solvents, chloroform, benzene or hexone is discussed.

Brown, Steinback and Wagner [1] have developed a method for lanthanides which can be selectively extracted from aqueous solution with acetylacetone at pH 4 to 6. Solubility and extractability of the acetylacetonates vary with the radius of the lanthanide ions. Extraction of the lanthanides with acetylacetone is enhanced by the decrease in basicity of the central metal ion.

Templeton and Peterson [36] carried out batch extractions of aqueous solutions of lanthanum(III) and neodymium(III) nitrate mixtures with n-hexyl alcohol at room temperature. A spectrophotometric method was employed to determine neodymium, and the total oxides were determined by ignition.

Dryssen and Dahlberg [9] have studied the extraction of lanthanum(III) samarium(III), hafnium(IV), thorium(IV) and uranium(VI) with oxine and cupferron. Two organic solvents were used, chloroform and methyl isobutyl ketone. The distribution of the metals between the two phases were measured radiometrically. The ionic strength in the aqueous phase was kept constant at 0.1 M using perchloric acid, sodium perchlorate, and sodium hydroxide. The complex formation constants were calculated. They also point out that the total metal concentration always was low ($<10^{-3} > 10^{-8}$M). If higher metal concentration had been used, the metal oxinates and cupferrates would have precipited at certain pH values.

Separations by extraction of certain lanthanide ions as 5,7-dichloro-8-quinolinol chelates are described by Moeller and Jackson [16]. The extraction of corresponding 5,7-dichloro-8-quinolinol chelates into chloroform was complete in controlled pH ranges. They also showed that it is favored by decreased basicity of the lanthanide ions. The quantities of material extracted were determined spectrophometrically.

An extraction and flame spectrophotometric method for the determination of lanthanum(III) was investigated by Rains and Dean [24].

Microgram quantities of lanthanum(III) were selectively extracted by a 0.1 M solution of 2-thenoyltrifluoroacetone in hexone from a 1 M acetate solution buffered at pH 5. Lanthanum(III) was determined by a flame photometer. Eighteen elements were tested for interferences.

Numerous papers have described the extraction of metal ions through complex formation with one of the organic esters of orthophosphoric acid or butyl derivatives. Warren and Suttle [37] have extensively studied the extraction of scandium(III), yttrium(III), and lanthanum(III) into an amyl alcohol solution containing the mono(n-alkyl) orthophosphoric acid from an aqueous nitric acid solution. The result was interpreted in terms of chelate formation of a four-membered ring.

Pollard, McOmie and Stevens [23] have reported a paper chromatographic method for the separation and detection of lanthanides. Individual lanthanons and lanthanon groups located at various spots on the paper were distinguished by using different spray reagents upon spots of the nitrates. Lanthanum(III) yielded a brightly green fluorescent spot when the dried strip was sprayed with morin in 50% alcohol, then exposed to ammonia and examined in ultraviolet light.

Lederer [12, 13], employing paper chromatography for the separation of ions, demonstrated the separation of such pairs of lanthanons as lanthanum-yttrium, lanthanum-dysprosium, and lanthanum-ytterbium using one solvent--ethanol containing 30% of 1 N hydrochloric acid or 10% of 2 N hydrochloric acid. The chromatogram was air-dried and dipped into an ammoniacal alcohol solution of 8-quinolinol and viewed under ultra-violet light. Lanthanum(III), and lutetium(III) yield yellow or green fluorescent spots while all others yield brown or black spots.

Morin has been used as a sensitive reagent for the fluorometric analysis or fluorometric detection of a large number of metals [2, 33].

Sandell [31, 32] has stated that morin gave a yellow-green fluorescence with beryllium(II) in a solution containing sodium hydroxide or potassium hydroxide.

Sill and Willis [34] have reported a fluorometric method using morin as chelating reagent for submicrogram quantities of beryllium(II) which produced fluorescence in alkaline solution. Experimental conditions have varied considerably, particularly with respect to instrumentation, quality and concentration of morin and alkalinity.

Thorium(IV) reacts with morin to yield a yellow complex that fluoresces when irradiated with ultraviolet light. This system has been investigated by Milkey and Fletcher [15]. The effect on the fluorescence by such variables as concentration of acid, alcohol, thorium, morin and complex, temperature and wavelength of exciting light are studied to determine experimental conditions yielding maximum fluorescence. The effects of zirconium(IV), aluminum(III), iron(III), calcium(II), and lanthanum(III) are discussed.

THEORETICAL

The possibility of using the distribution method to study complex compounds in solutions and the feasibility of separating substances by this method was demonstrated a long time ago. The general practical quantity in describing extraction or separation is the distribution ratio, D, a stoichiometric ratio including all species of the same component in respective phases, is defined as follows,

$$D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}}$$

Another quantity which indicates the degree of separation obtainable and which is related to D, is the percent extraction E. It is defined as follows,

$$E = \frac{100[A]_0 V_0}{[A]_0 V_0 + [A]_w V_w} = \frac{100D}{D + V_w/V_0}$$

where

A = concentration of a substance and o and w refer to the two solvents

V = solvent volume

In inorganic extraction systems, complexing of metal ions by organic complexing agents leads to the formation of uncharged species which fall into two main categories, chelates and ion association systems.

Chelate extraction systems include only those involving neutral chelates. The case may be described by

$$M^{n+} + nR^- \rightleftharpoons M R_n$$

where

M^{n+} = n-valent metal ion

R^- = an anion of a suitable chelating agent

In association extraction, the metal ion combines with a molecule or ion to form a positively or negatively charged ion. This charged species then forms an effective neutral ion pair with other ions. These possible interactions are shown by the following equations,

$$M^{n+} + bB \rightleftharpoons M B_b^{n+}$$

$$M B_b^{n+} + nX^- \rightleftharpoons (M B_b^{n+}, nX^-)$$

or

$$M^{n+} + (n + a) X^- \rightleftharpoons MX_{n+a}^{a-}$$

$$MX_{n+a}^{a-} + aY^+ \rightleftharpoons (aY^+, MX_{n+a}^{a-})$$

where

B = neutral ligand

X^- = an anion appropriate for pairing with the cation

Y^+ = a suitable cation required to form the ion-pair

From a quantitative standpoint, consideration of equilibria existing in the extraction system is helpful in pointing out which experimental parameters play an important role in the completeness as well as the selectivity of the extraction. Although a chelate extraction was chosen to represent the inorganic type, the same general approach may be used for ion association extraction [20]. The ionization and complexation reactions, and the distribution of various species and the pertinent respective equilibrium constants can be represented by the following condensed expressions (HR will serve as a general formula for the reagent),

$$H^+ + R^- \rightleftharpoons HR \rightleftharpoons HR$$

$$M^{n+} + nR^- \rightleftharpoons MR_n \rightleftharpoons MR_n$$

water | organic solvent

The chelating reagent distributes between the two phases

$$HR_{aq} \rightleftharpoons HR_{org} \qquad K_{Dr} = \frac{[HR]_o}{[HR]_w}$$

the reagent dissociates in the aqueous phase

$$HR \rightleftharpoons H^+ + R^- \qquad K_a = \frac{[H^+][R^-]}{[HR]}$$

to give a chelating anion R^- which reacts with the metal ion and forms the extractable chelate

$$M^{n+} + nR^- \rightleftharpoons MR_n \quad K_f = \frac{[MR_n]}{[M^{n+}][R^-]^n}$$

which in turn, distributes between the phases

$$MR_n \rightleftharpoons MR_{n(org)} \qquad K_{D_x} = \frac{[MR_n]_o}{[MR_n]_w}$$

Therefore, the distribution ratio D, can be evaluated from these equilibrium expressions. Thus,

$$D = \frac{(M)_o}{(M)_w} = \frac{[MR_n]_o}{[M^{n+}]_w} = \frac{K_f K_a{}^n K_{D_x}}{K_{D_r}} \cdot \frac{[HR_o]^n}{[H^+]^n_w}$$

It may be noted from the equation above that the extractability of a metal ion with given reagent and organic solvent depends greatly upon the organic phase concentration of the reagent and the hydrogen ion concentration in the aqueous phase. An increase in the reagent concentration in the organic phase or a decrease in the hydrogen ion concentration in the aqueous phase will increase the distribution ratio D.

Also, the equation indicates that D is dependent directly on the chelate stability (K_f), the relative solubility of the chelate in the organic phase (K_{D_x}), the reagent dissociation in the aqueous phase (K_a) and inversely on the extent of extraction of the undissociated organic reagent into the organic phase (K_{D_r}).

If several species can be formed between ion and a complexing agent and several species are extracted into the organic phase, an extremely complex relationship among the extraction parameters exists. The general pattern for ion association extraction is not suitable for describing this extraction.

EXPERIMENTAL

Instrumentation

Extraction separatory funnels with "Teflon" stop-cocks were used for the entire extraction procedures.

The spectrofluorometer employed in this study was the same one used by Fleck [10] in this laboratory, also the same procedure employed in obtaining fluorescence intensity measurements. The only change was that the entrance slit of the Bausch and Lomb monochromator, and the exit slit of the Beckman D.U. were set to 1.0 mm. The Bausch and Lomb monochromator was set at 365 mμ for all measurements. The instrument was calibrated with 0.4 γ per ml. dichlorofluorescein standard solution. Beckman D.U. sensitivity was adjusted when this solution was excited in the 10x20x50 mm. silica cell so that a fluorescence intensity of 50 was attained.

A Beckman DK-2 spectrophotometer was used for all absorption measurements. Matched one cm silica cells were employed in all these measurements.

A Beckman model G pH meter with a glass-saturated calomel electrode pair was used to measure pH of the aqueous phase. The meter was standardized at pH 4 with Beckman standard buffer solution.

Reagents

Lanthanum sesquioxide -- Optical grade, Heavy Mineral Co., Chattanooga, Tennessee

Samarium sesquioxide -- Labeled purity 99.9 per cent, Michigan Chemical Corporation, St. Louis, Michigan

Dichlorofluorescein -- Eastman Kodak, white label.

Morin -- Reagent grade. Lot 8861, K & K Laboratories, Inc.
Methyl isobutyl ketone -- Eastman Kodak, C. P.
Perchloric acid -- 70-72 per cent Bakers Analyzed Reagent.
Hydrochloric acid -- A.C.S. Baker Analyzed Reagent.
Sulfuric acid -- A.C.S. DuPont Analyzed Reagent.
Nitric acid -- A.C.S. DuPont Analyzed Reagent.
Sodium bicarbonate -- A.C.S. Fisher Certified Reagent.
Ammonium hydroxide -- A.C.S. Baker Analyzed Reagent

Hexone (methyl isobutyl ketone or 4-methyl 2-pentanone) of technical quality was purified by the procedure of Rydberg and Brita Bernstron [30]. The solution was filtered and was washed with sodium bicarbonate and water to remove acid and water soluble impurities. Then the solution was saturated with water overnight, and distilled. A 103° to 104° C fraction was collected and the purified hexone was stored in an amber colored screw capped bottle.

The distilled water used throughout this investigation was passed through a "crystalab Deeminizer" ion exchange column in order to remove possible metal ion impurities contained in the water.

Preparation of Reagent Solutions

All stock solutions of lanthanum(III) perchlorate, sulfate, nitrate and chloride or samarium(III) perchlorate were prepared by dissolving the required amounts of freshly ignited oxides in 1 M perchloric acid, sulfuric acid, nitric acid or hydrochloric acid. The concentrations were as follows:

La(III) in perchloric acid . . . . . 0.326 mg per ml
La(III) in sulfuric acid . . . . . 13.2 mg per ml
La(III) in nitric acid . . . . . 14.3 mg per ml
La(III) in hydrochloric acid . . . . . 13.2 mg per ml
Sm(III) in perchloric acid . . . . . 3.5 mg per ml

Working solutions were prepared from the stock solution by dilution with "deeminized" water.

Solution of morin of the desired concentrations were prepared by dissolving a weighed quantity of the solid material in purified hexone. Fresh reagent solution was prepared for every trial.

Fluorometric procedures were standardized with 0.4γ per ml. solution of dichlorofluorescein in four percent ethanol. The standard solution was prepared by dissolving a 4 mg. quantity of reagent in 1 l. 95 percent ethanol. A 10 ml. aliquot of this stock solution was diluted to 100 ml. for the working solution.

Experimental Procedures

All experimental work in this investigation was carried out at room temperature, 26 ± 1° C. A variety of solvents under various experimental conditions was examined for the purpose of finding a method for quickly and efficiently extracting lanthanum(III) from aqueous solution. Organic solvents tested were chloroform, cyclohexanol or hexone. But of these only hexone showed any promise, and therefore the procedures which follow, pertain to this solvent. The remaining solvents were tested by similar procedures and reasons for rejecting these are given in the discussion section.

All standard metal ion solutions were prepared by dilution. The concentrations are expressed in units of micrograms, γ, per 10 ml. of solution.

A 10 ml. aqueous sample solution containing a fixed amount (4 - 64γ) of lanthanum(III) was transferred with a volumetric pipet to a separatory funnel, 20 ml. (containing 100 - 800γ morin) of the organic reagent morin in hexone was added. The solution was mixed thoroughly. Finally the pH of the aqueous phase was adjusted to the desired level

with dilute ammonia or dilute perchloric acid. The funnel was shaken for three minutes. The phases were allowed to separate. Within a 30 minutes period, two clear layers were formed. The organic layer was yellow in color and water layer colorless. The respective layers were transferred to individual glass stoppered 25 ml. flasks. The pH of the aqueous phase was measured. Aliquots of the organic phase were taken out for spectrophotometric and spectrofluorometric measurements.

Absorption spectra of the lanthanum(III)-morin complex in hexone were measured over the range from 270 mμ to 700 mμ. The entire spectrum was run against hexone as a comparison liquid.

For fluorescence intensity measurements, a portion of the organic phase was excited with 365 mμ radiation, and the intensity of the fluorescence emitted at 505-510 mμ was measured. With each set of extractions, a blank was carried through a similar procedure. The blank was merely very dilute perchloric acid. Its pH was that of the aqueous sample solution.

To test for completeness of extraction, three successive extractions of individual aqueous aliquots were performed. For the first extraction 20 ml. of morin reagent solution was used, for the second 15 ml. of morin reagent and 5 ml. of hexone and for the third 10 ml. of morin reagent and 10 ml. of hexone. In all extractions, a total of 20 ml. of hexone was present.

EXPERIMENTAL RESULTS AND DISCUSSION

Solvents Tested

In preliminary investigation, a variety of organic solvents such as chloroform, cyclohexanol and hexone were tested in search for an effective solvent for the extraction of lanthanons from aqueous solutions. Chloroform was not suitable because of the low solubility of morin in this solvent.

When morin dissolved in purified cyclohexanol was added to dilute perchloric acid solutions containing lanthanum(III) and the pH adjusted for optimum complexation reaction with dilute ammonia, stable emulsions in both phases were formed. In some trials, the emulsion was stable for twenty-four hours. Better separation of the phases was attained when dimethylformamide, dioxane or acetone was added. But when these mixed solvents were employed, the fluorescence intensities for the organic phase of the blank solutions were almost as high as those obtained with the organic phases separated from solution containing the reagent and lanthanum(III). Only small wavelength separations between the absorption peaks recorded with the organic phases from the blank and sample solutions were noted at all pH levels tested. Such information would lead to the conclusion that complexation of lanthanum(III) by morin does not occur to any great extent in the above media. Investigations employing cyclohexanol as the extracting solvent were discontinued.

Hexone was the most satisfactory solvent for the desired extraction. With hexone a low and reproducible fluorescence intensity for the blank solution was obtained, and only a thirty-minute period was required for the separation of the aqueous and organic phases.

Since the distribution ratio in a liquid-liquid extraction is a concentration ratio, the actual fraction of the total solute extracted will vary with the ratio solvent volumes [21]. The selected volume ratio of organic to aqueous phase was 2 to 1 throughout this entire investigation.

Volume ratios of 1:2, 1:1 and 3:1 were also tested. Six hours after shaking, an emulsion still persisted in the 1:2 system and the organic phase yielded an uncertain fluorescence intensity reading of 36.5. Good separation was attained in the 1:1 and 3:1 systems. Fluorescence intensity readings for the organic phases were 56.5-61.2 and 32.5-34.0 respectively, in duplicate trials. Even though higher fluorescence intensity readings were obtained with the organic phase from the 1:1 systems, more reproducible intensity readings were obtained with the organic phase from the 2:1 volume ratio system and was therefore used throughout this investigation.

Effect of pH

The extractability of metal complex is greatly influenced by the pH of the aqueous phase. Extraction as a function of pH was studied. The organic phase was analyzed after extraction by spectrophotometric and fluorometric measurements. To investigate this effect, a series of solutions containing 32γ of lanthanum(III) with pH ranging from 2 to 10 was prepared. To each of these 400γ of morin in 20 ml. of hexone had been added and the extraction performed. In Figure 1, curve A shows that maximum fluorescence intensity I_{365}^{505} from the complex in the organic phase is attained when the pH is 6.7-6.8. Curve B shows that morin in the organic phase obtained from the extraction of the blank does not fluoresce appreciably until a pH of 8-9 in the blank is reached.

In Figure 2, curve A shows the effect of pH on the absorbance of the organic phase containing the lanthanum(III)-morin solution at 410 mμ.

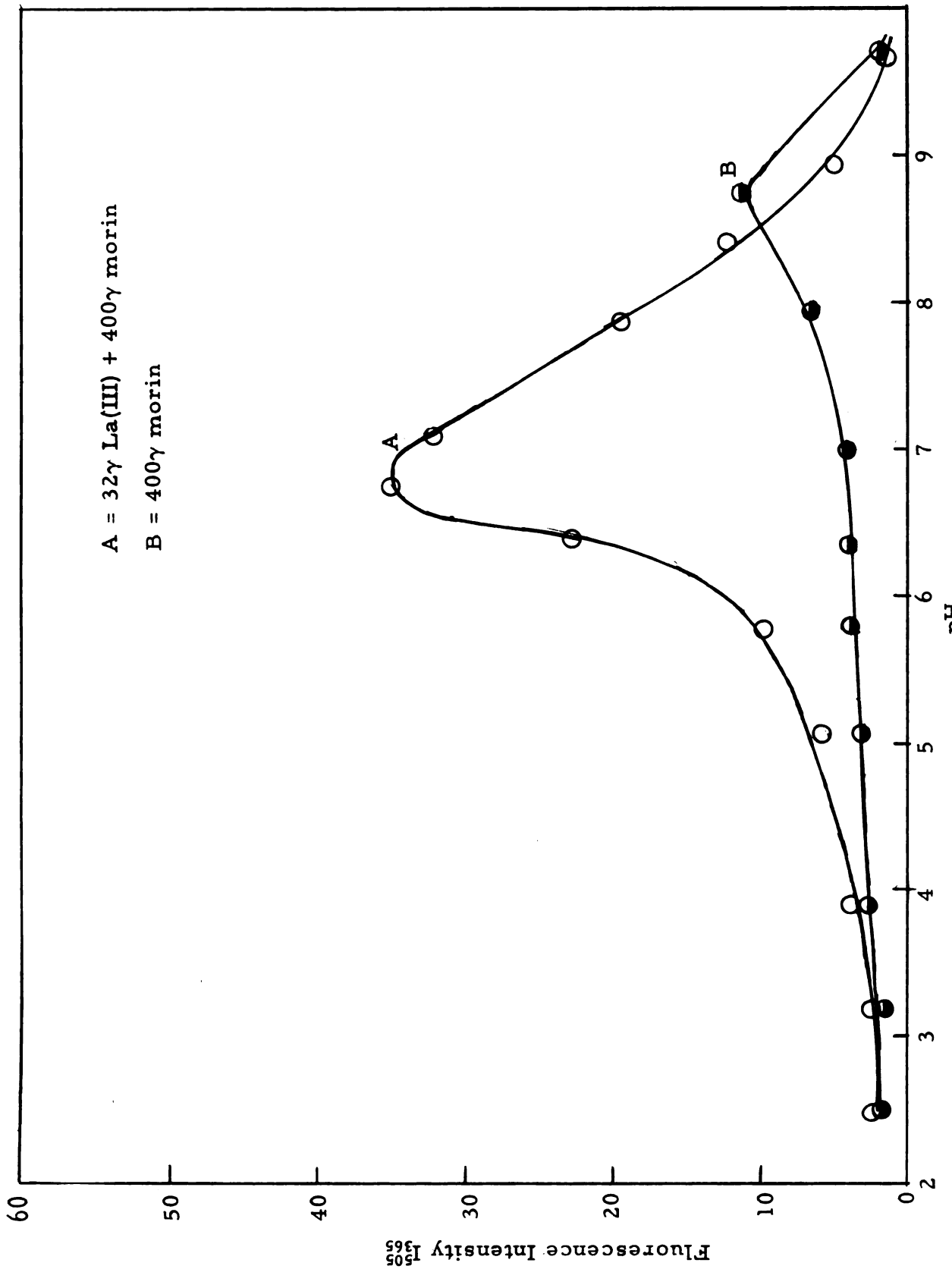


Figure 1. Effect of pH in the aqueous phase on fluorescence of hexone phase containing La(III)-morin complex or morin.

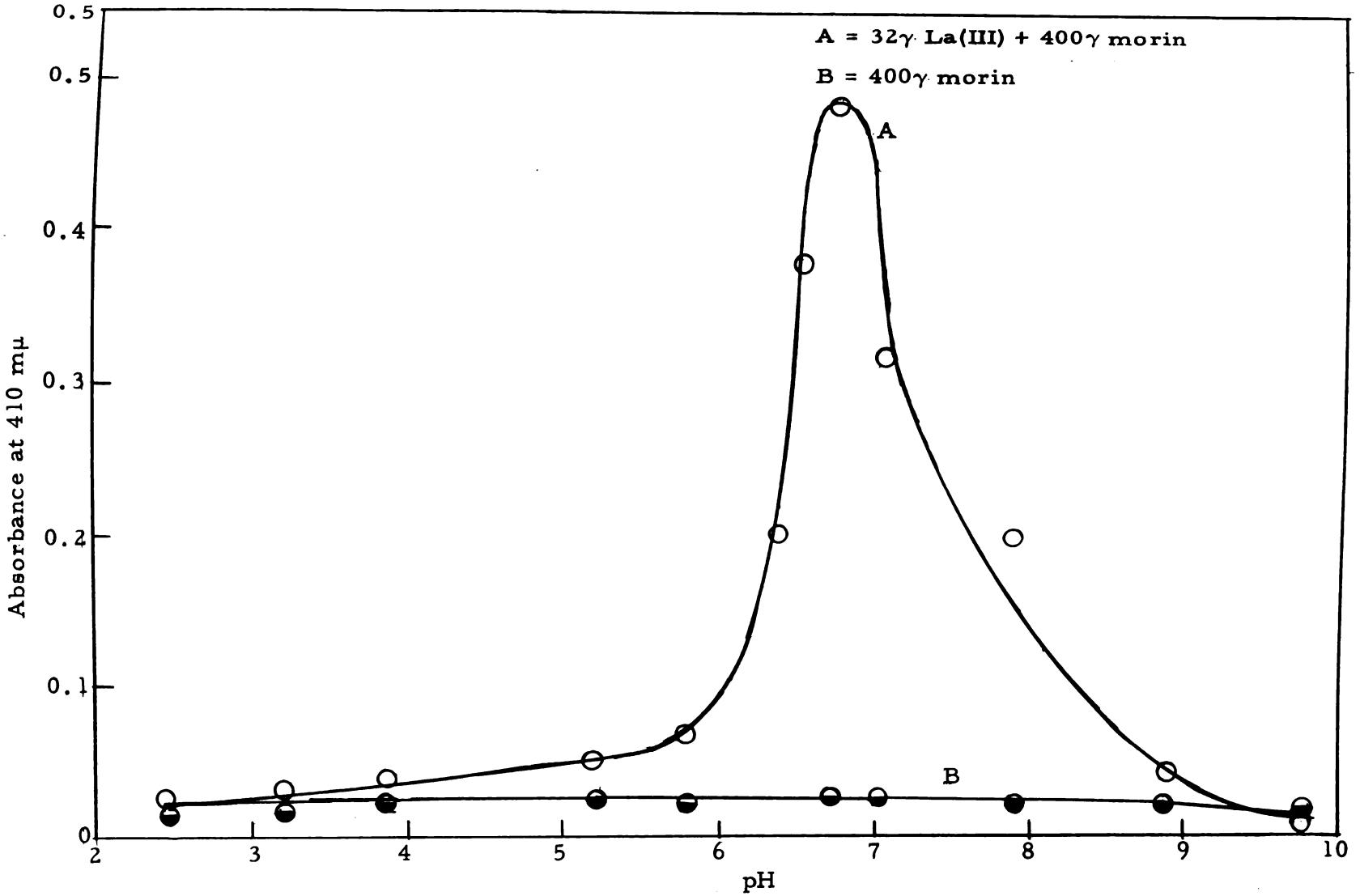


Figure 2. Effect of pH in the aqueous phase on the absorbance of hexone phase containing La(III)-morin complex or morin.

The absorbance of the lanthanum(III)-morin solutions reach a maximum at pH 6.7-6.8 and then decrease. Above pH 8, the absorption peaks shift to a longer wavelength. It is suggested that another non-fluorescent species is being formed. Curve B shows that morin in the organic phase obtained from the extraction of the blank of pH 2 to 10 does not absorb appreciably at 410 mμ. In subsequent studies the pH of the aqueous sample solutions was adjusted to pH 6.7 to 6.8 before the extraction.

In Figure 3, curves A and B show the absorption spectra for solutions of pure morin and the lanthanum(III)-morin complex in the organic phase obtained from the extraction at pH 6.7 to 6.8, while curves C and D show the fluorescence spectra for pure morin and lanthanum(III) + morin complex solutions.

Effect of Lanthanum(III) Concentration

The effect of increasing lanthanum(III) concentration in the aqueous phase at pH 6.7-6.8 on the fluorescence and absorbance of the organic phase, when the original morin content in the hexone was kept at 400γ, is shown in Figure 4. Curves A and B indicate that a nearly linear increase in the fluorescence and absorbance for the lanthanum(III)-morin hexone solutions is attained for the concentration range of 0 to 48γ of lanthanum(III) in the original sample solution. The slopes of both curves decrease sharply at a lanthanum(III) concentration of above 48γ. This behavior suggests that the complex is relatively weak and/or that the limit of extractability was reached. This study indicated that 32γ of lanthanum(III) would be used in the preparation of solutions to study various effects on extractability and fluorescence to ensure that the maximum amount of lanthanum(III) would be converted to the complex form which would be extracted.

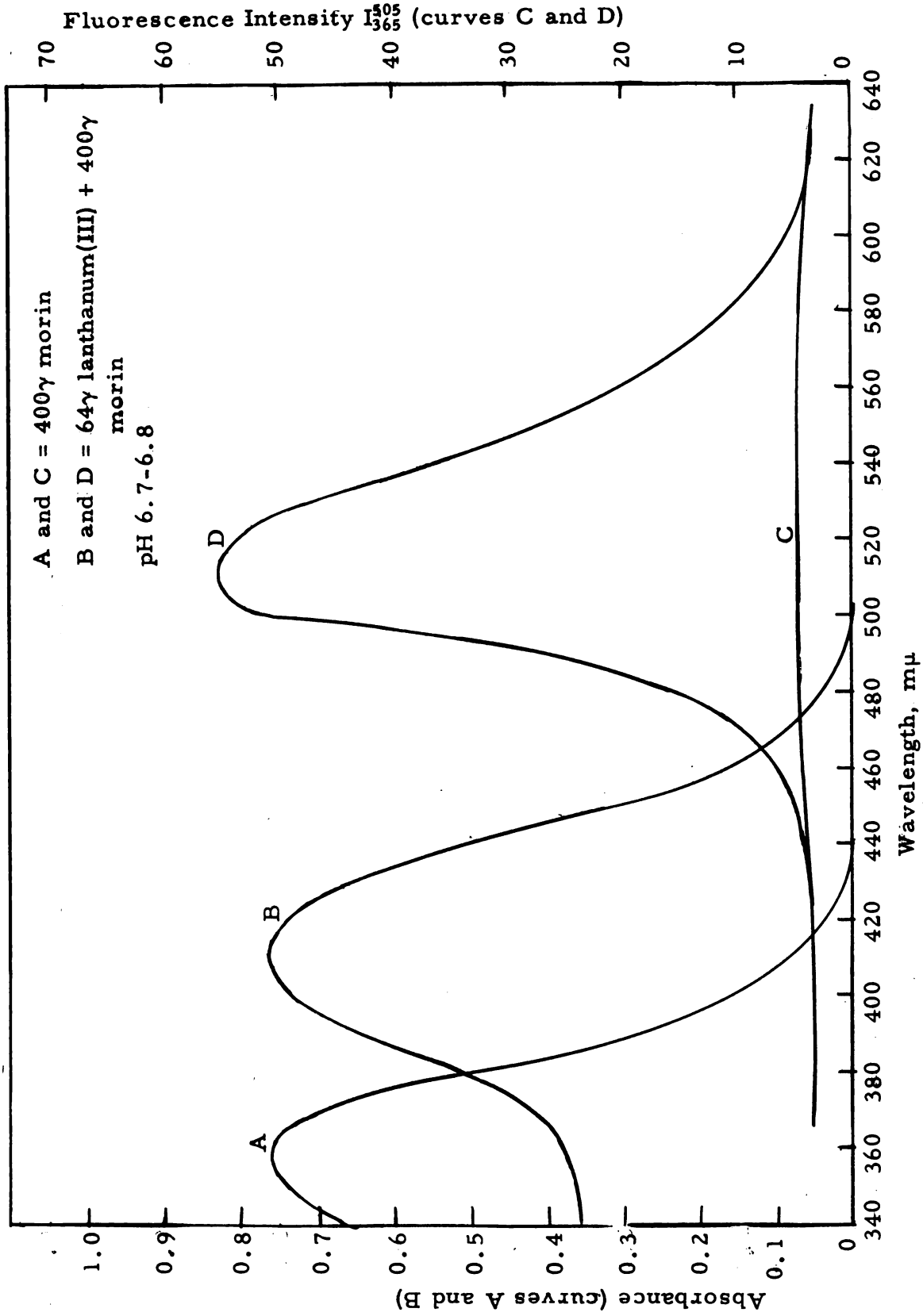


Figure 3. Asborption and fluorescence intensity curves for lanthanum(III)-morin complex and morin in hexone.

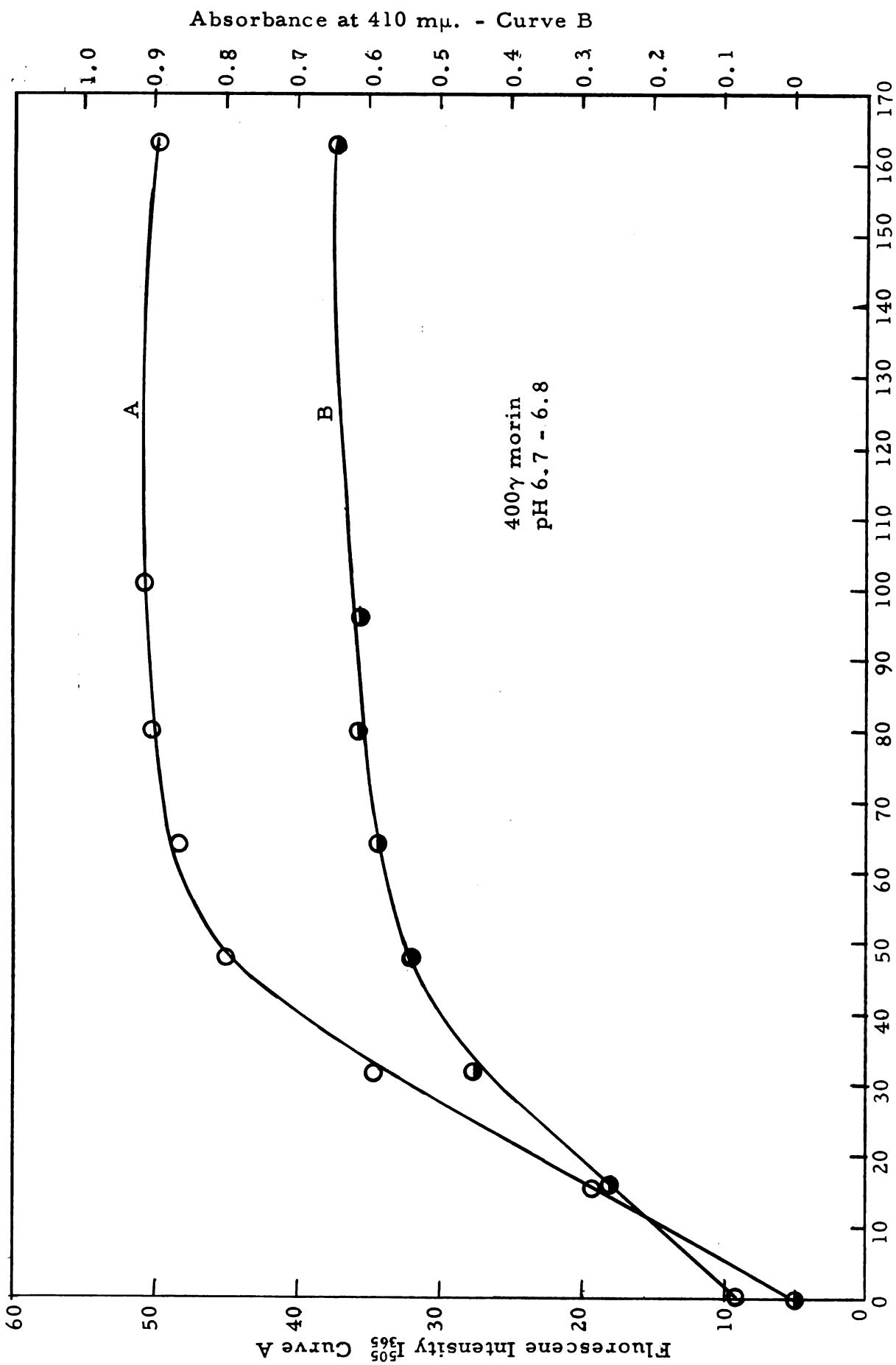


Figure 4. Relationship between lanthanum(III) concentration in the aqueous phase and absorbance or fluorescence intensity of hexone phase.

Effect of Morin Concentration

Figure 5, curve A shows the effect of the change of morin concentration in the hexone reagent solution on the fluorescence of the organic phase when the original aqueous phase contains 32γ of lanthanum(III) at pH 6.7 to 6.8, while curve B shows the same effect on the absorbance. Maximum fluorescence is obtained from the organic phase containing 300γ to 400γ of morin reagent per 20 ml. of hexone. On further increase of morin concentration the fluorescence intensity decreases. This effect may be due to the absorption of the exciting light by the non-fluorescent uncombined morin in solution. Curve B shows that there is a nearly linear increase in absorbance with increasing morin concentration up to 400γ morin per 20 ml. of hexone and on further increase in morin concentration the absorbance still increases but at a lower rate. This is due to the absorption by the morin which absorbs 410 mμ radiation but with lower absorptivity than that of the complex.

Effect of Samarium(III)

Figure 6 shows the effect of the addition of samarium(III) to the aqueous phase containing 32γ lanthanum(III) when the pH is 6.7-6.8 on the fluorescence of the organic phase which originally contained 400γ of morin. Curve A shows that the fluorescence intensity increases slightly when samarium(III) content in the aqueous sample solution is varied from 0 to 20γ. It is suggested that a small amount of fluorescent species is being formed. When an extraction was carried out on an aqueous sample containing only 20γ of samarium(III), a fluorescence intensity from the organic phase of approximately two units was observed. Above 20γ of samarium(III), the fluorescence intensity decreases slightly and this is probably due to the competition between

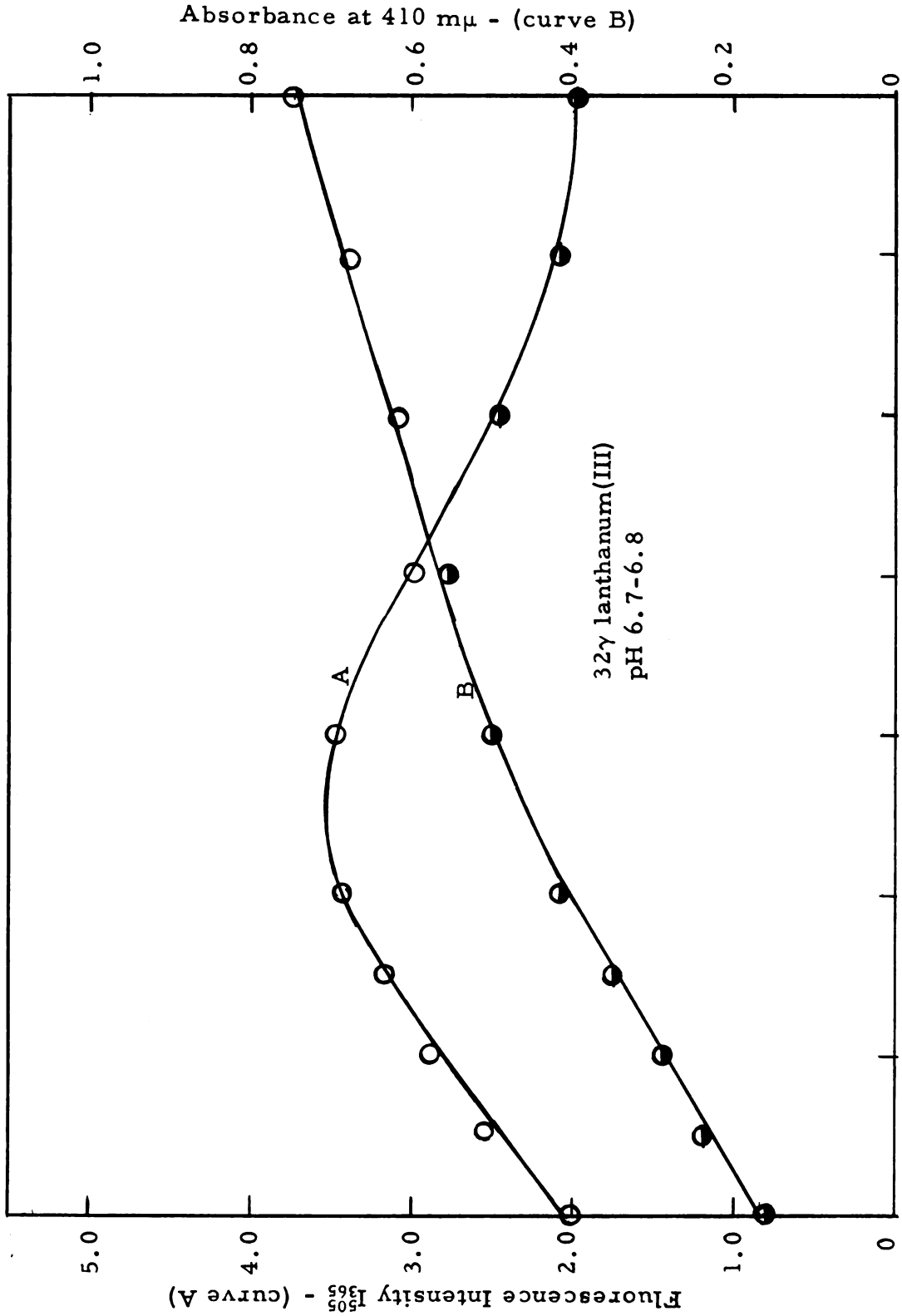


Figure 5. Relationship between morin content in hexone (reagent) and absorbance or fluorescent intensity of hexone phase.

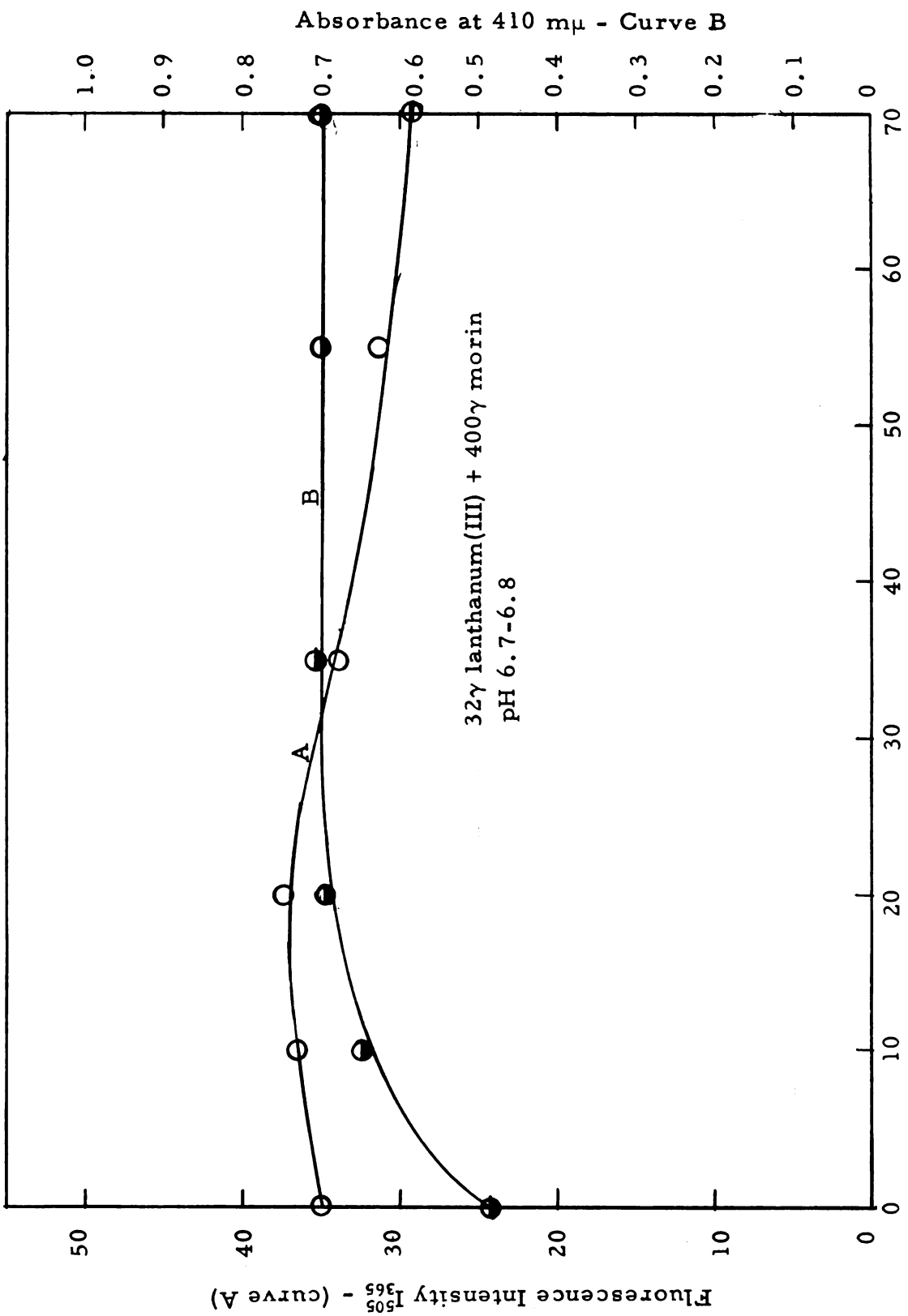


Figure 6. Effect of samarium(III) on absorbance and fluorescence intensity of the hexone phase containing lanthanum(III)-morin complex.

samarium(III) and lanthanum(III) for morin. Curve B indicates that the absorbance increases with increasing concentration of samarium(III) from 0 to 20γ, then remains essentially constant above 20γ of samarium(III). This study shows that samarium(III) has more effect on fluorescence at extremely dilute aqueous lanthanum(III) levels and high organic reagent concentrations.

Effect of Acid

Table 1 demonstrates the possibility of extraction of lanthanum(III) from a dilute hydrochloric, nitric acid or sulfuric acid solution at pH 6.7-6.8 into hexone by employing 400γ of morin in hexone.

The general shape of the absorption and fluorescence curves for the organic phases is the same as that obtained from perchloric acid sample solutions in all cases. This study indicates that similar complexes are extracted into the organic phase. Nitrate, chloride, sulfate or perchlorate ions do not compete strongly with morin for lanthanum(III) and in their presence extractable ion-pairs with lanthanum(III)-morin and some anion are still formed. No significant difference in extractability of lanthanum(III) is attained from any one of these dilute acid solutions.

Completeness of Extraction

Figure 7, curve A, B and C show the completeness of extraction on the fluorescence of the organic phase when aqueous solutions containing various amounts of lanthanum(III) at pH 6.7-6.8 are extracted with successive portions of morin reagent (400γ, 300γ or 200γ in 20 ml. of hexone). The results indicate that the major part of the lanthanum(III) in the aqueous solution is extracted with the first portion of morin

Table 1. Extraction of Lanthanum(III) from Different Media at pH 6.7-6.8 by Morin-hexone

Dil. Acid	La(III), γ	Abs., 410 mμ	Fluor., I_{365}^{505}
HCl	13.2	0.290	14.5
HCl	26.2	0.515	32.5
HNO_3	14.3	0.225	11.1
HNO_3	28.6	0.530	31.5
H_2SO_4	13.2	0.260	12.0
H_2SO_4	26.6	0.530	27.0

reagent (400 γ morin) and also that up to 28γ of lanthanum(III) are extracted completely by this single extraction. The second portion of the morin reagent (300γ morin) is effective for completing the extraction when the concentration of lanthanum(III) is between 28 and 48γ in the sample solution. A third portion of morin reagent (200γ morin) was used. No significant extraction was accomplished by this step.

Results from these experiments were also used to test the reproducibility in extraction. Curve A of Figure 7 is essentially a calibration curve for lanthanum(III) determination by a single extraction. It is the best curve obtained when the respective fluorescence intensities for the organic phase from the sample solutions were plotted against the concentrations of lanthanum(III) in the sample solutions. The difference between the lanthanum(III) concentration present in each of the sample solutions and that found by using curve A, to read off the concentration corresponding to the fluorescence intensity measured for each of the samples, is listed in Table 2 for the 24 solutions tested.

Only three attempts yielded absolute deviations greater than 2γ. With better temperature control and standardization in experimental procedure, the deviations could undoubtedly be minimized.

Stability of the Complex in the Organic Phase

The color of the organic phase was fairly stable. When the hexone extract containing the lanthanum(III)-morin complex was stored in a dark place for a period of twenty-four hours, no appreciable change in its absorption or fluorescence was produced.

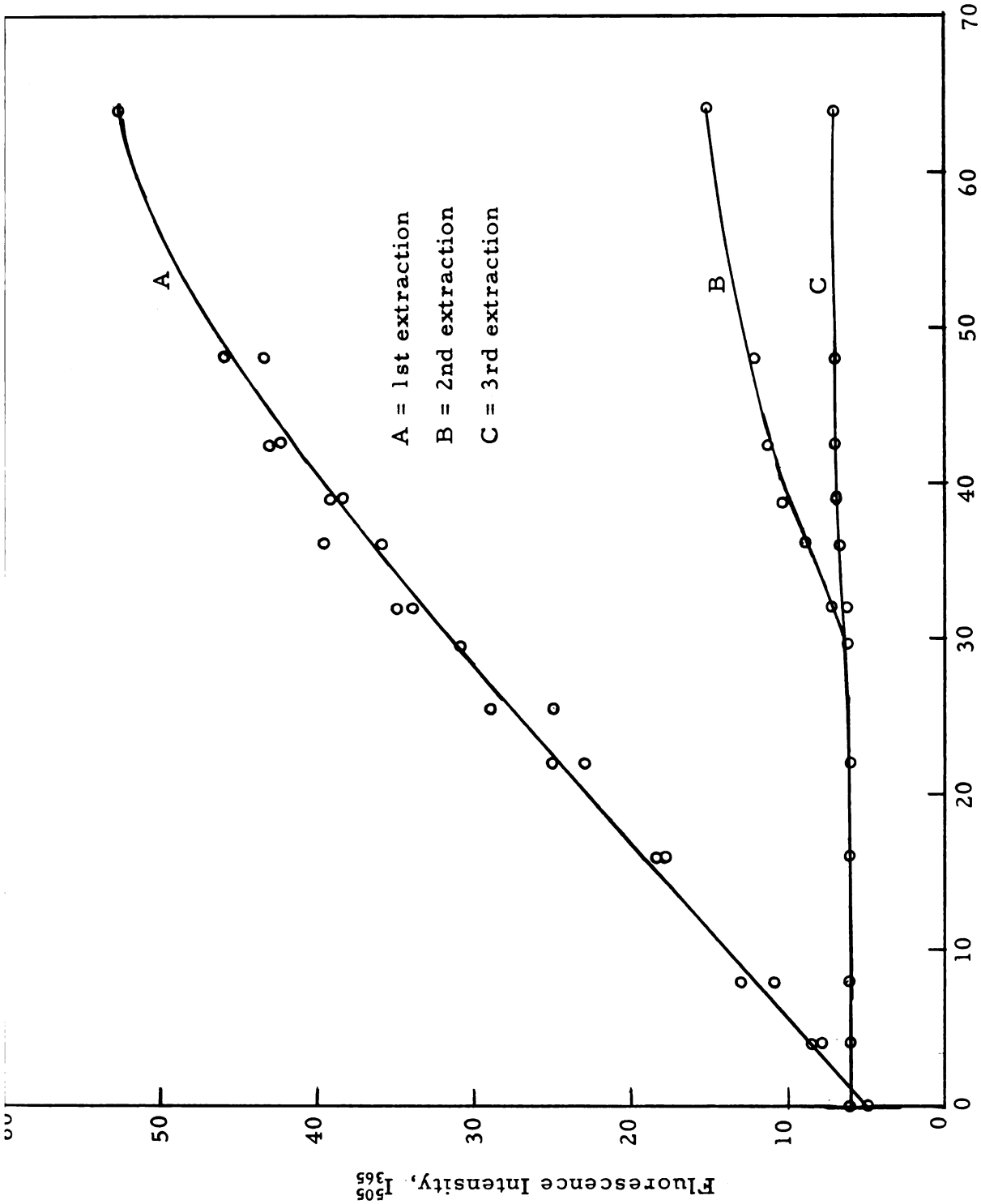


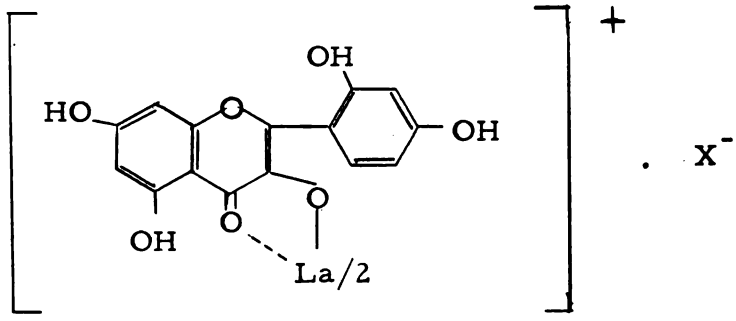
Figure 7. Effectiveness of each of three successive extractions performed on individual sample solutions.

Table 2. Lanthanum(III) Recovery by a Single Extraction with Morin-Hexone from Aqueous Perchloric Acid Sample Solutions at pH 6.7-6.8

Sample	Lanthanum(III), γ		Absolute Diff., γ	Relative Deviation p.p.h.
	Taken	Found		
1	0	0	0	0
13	0	0	0	0
2	4.0	4.0	0	0
14	4.0	3.0	-1.0	25
3	8.0	6.5	-1.5	23
15	8.0	9.0	+1.0	12
4	16.0	14.5	-1.5	19
16	16.0	15.0	-1.0	6
5	22.0	20.0	-2.0	9
17	22.0	22.0	0	0
6	25.5	22.5	-3.0	12
18	25.5	27.0	+1.5	6
7	29.0	29.0	0	0
19	29.0	29.0	0	0
8	32.0	32.5	+0.5	2
20	32.0	34.0	+2.0	6
9	36.0	35.5	-0.5	1
21	36.0	40.0	+4.0	10
10	39.0	38.5	-0.5	1
22	39.0	39.0	0	0
11	42.5	43.5	+1.0	2
23	42.5	44.0	+1.5	3
12	48.0	45.5	-2.5	5
24	48.0	48.5	+0.5	1

Nature of the Complex

No attempt was made to obtain information on the nature of the complex. The absorption curve and the fluorescence spectrum curve for the lanthanum(III) species extracted into hexone are identical with those obtained by Fleck [10] with the lanthanum(III)-morin complex in a 50-50 dioxane-water solution. By a continuous variation method and a slope ratio method he established that the species was a 1:2 complex, lanthanum(III) to morin, and that a probable structure could be



Such a charged species could only be extracted into an organic solvent as an ion-pair. Since lanthanum(III) combines readily with hydroxide ion, it is not unreasonable to assume that the extracted species would be the ion-pair formed between the complex and a hydroxide ion. It is also possible that the ion pair could consist of the lanthanum(III)-morin complex and the anion, such as perchlorate or chloride, which is present in the aqueous phase. No experimental evidence was obtained in this study to establish the nature of the extracted species.

CONCLUSION

Lanthanum(III) forms with morin a complex which can be extracted quantitatively into hexone by a single extraction when the pH in the aqueous phase is adjusted to 6.7 to 6.8. The selected volume ratio of organic to aqueous phase was 2 to 1 (20 ml. of hexone containing 400γ of morin to 10 ml. of lanthanum(III) in dilute perchloric acid solution).

In the absorption spectrum for the solution of lanthanum(III)-morin complex in hexone, the maximum absorption peak is at 410 mμ, while for pure morin hexone solution, the peak falls at 356 mμ, but it also absorbs to a small extent at 410 mμ. Pure morin hexone solution does not absorb beyond 450 mμ, therefore the complex content in hexone could be determined at 450 mμ.

The lanthanum(III)-morin complex in hexone fluoresces when it is excited with 365 mμ radiation, and the fluorescence radiation is emitted at 505-510 mμ. Pure morin hexone solution obtained from the extraction of blank does not fluoresce when the pH of the aqueous blank is 8.

When aqueous solutions containing various amounts of lanthanum(III) at pH 6.7 to 6.8 were extracted with successive portions of morin reagent (400γ, 300γ or 200γ in 20 ml. of hexone), the fluorescence intensity of the organic phase showed that the major part of the lanthanum(III) in the aqueous solution was extracted with the first portion of morin reagent (400γ morin) and also that up to 28γ of lanthanum(III) can be extracted completely by this single extraction. The second portion of morin reagent (300γ morin) is effective for completing the extraction up to the concentration between 28 to 48γ of lanthanum(III) in the aqueous solution.

The possibility of extracting lanthanum(III) from an aqueous dilute hydrochloric acid, nitric acid or sulfuric acid solution of pH 6.7 to 6.8 into hexone containing 400γ morin was studied. The absorption and fluorescence curves for the organic phase show that complexes identical to the one extracted from the perchloric acid solution, are extracted into the organic phase.

A linear relationship was obtained between the absorbance or fluorescence intensity of the lanthanum(III)-morin hexone solutions and lanthanum(III) concentration when the concentration of lanthanum(III) in the aqueous layer was varied from 0 to 48γ. The slopes of both curves decrease sharply above the concentration of 48γ of lanthanum(III). This behavior suggests that the complex is relatively weak and/or that the limit of extractability is reached.

The effect of samarium(III) in the original aqueous phase containing 32γ of lanthanum(III) shows that samarium(III) has a slight effect on the fluorescence intensity of the organic phase at very dilute aqueous lanthanum(III) levels from 0 to 20γ. Above 20γ, the fluorescence intensity decreases slightly probably due to the competition between samarium(III) and lanthanum(III) for morin. Absorbance increases with increasing concentration of samarium(III) up to 20γ, then remains essentially constant above 20γ of samarium(III).

No attempts were made to obtain information of the nature of the complex in the organic phase. It is assumed that the extracted species would be the ion-pair formed between the lanthanum(III)-morin and a hydroxide ion or perchlorate ion.

This study was a preliminary investigation of the extraction of lanthanum(III) with morin into hexone. Since this study was carried out with solutions of very low ionic strength, it would be interesting to test how the system would behave at high ionic strength. It would also be interesting to determine the nature of extracted species by evaporating

the solvent and identifying the crystals obtained. In further studies, the extractability of all available lanthanide ions by morin in hexone could be tested.

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