A SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDY OF SOME LANTHANIDE (III)-MORIN COMPLEXES

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY Ronald H. Van Eenenaam

25170421

THESIS





LIBRARY Michigan State University

•



PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE	
		·	
MSU is An Affirmative Action/Equal Opportunity Institution			

ABSTRACT

A SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDY OF SOME LANTHANIDE (III)-MORIN COMPLEXES

by Ronald H. Van Eenenaam

Morin forms complexes with dysprosium (III), erbium (III), europium (III), holmium (III), and ytterbium (III) which do not fluoresce significantly. The various factors which effect the absorbance of these complexes in 50 percent dioxane-50 percent water and the nature of these complexes were investigated.

Morin forms a 1:2 complex (lanthanide (III) : morin) with europium (III) at pH 5.50, and with dysprosium (III), holmium (III), erbium (III) and ytterbium (III) at pH 5.00. The values of the equilibrium ratios for these complexes are 15.1, 19.4, 20.9, 24.6 and 31.5, respectively.

The complexes fluoresce only slightly more than morin when exposed to 365, 405 or 436 m μ . radiation, while the complexes of lanthanum, gadolinium and lutetium fluoresce under these conditions.

The absorption band peak of morin occurs at 356 m μ ., while the complex absorption band peaks for europium, dysprosium and erbium, holmium and ytterbium occur at 408, 414 and 419 m μ ., respectively.

A single isoabsorptive point exists in the absorption spectra of each of the complexes. The isoabsorptive point for the europiummorin system occurs at 376 mµ., the erbium-morin and ytterbiummorin systems at 380 mµ., the dysprosium-morin system at 382 mµ., and the holmium-morin system at 388 mµ.

The absorbances for the complexes change linearly with change in lanthanide (III) concentration over the approximate concentration ranges, 0 to 1.4×10^{-5} M., in the presence of excess morin, 1.32×10^{-4} M.

The ionic strength effect by sodium perchlorate, up to 0.1 M., was negligible.

A SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDY OF SOME LANTHANIDE (III)-MORIN COMPLEXES

By

Ronald H. Van Eenenaam

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Andrew Timnick for guidance and encouragement throughout this investigation and course of study.

VITA

Name: Ronald H. V	an Eenenaam
Born: April 8, 193	9 i n Holland, Michigan
Academic Career:	Holland High School, Holland, Michigan (1954-1957)
	Hope College, Holland, Michigan (1957-1961)
	Michigan State University, East Lansing, Michigan (1961-)

Degree Held: A. B. Hope College (1961)

1
11
Н
E
DI
517
50
LIJ
AP
1

TABLE OF CONTENTS

Pag	je
INTRODUCTION	1
HISTORICAL	6
EXPERIMENTAL	9
INSTRUMENTATION 1	0
REAGENTS	2
PREPARATION OF REAGENT SOLUTIONS 1	3
EXPERIMENTAL PROCEDURES 1	5
Method of Sample Preparation	5
Instrumental Measurements I Nature of the Complex I	.5
DISCUSSION OF RESULTS	8
General	9 9 9
SUMMARY AND CONCLUSIONS	3
LITERATURE CITED	6
$\mathbf{APPENDIX} \dots \dots$	5

•

LIST OF FIGURES

FIGURE		Page
1.	Block diagram of spectrofluorometer	. 11
2.	Absorption spectra of morin and the complexes of morin with dysprosium (III) and erbium (III) in 50-50 DW at pH 5.00	. 20
3.	Absorption spectra of morin and the complexes of morin with holmium (III) and ytterbium (III) in 50-50 DW at pH 5.00	21
4.	Absorption spectra of morin and the complex of morin with europium (III) in 50-50 DW at pH 5.50	. 22
5.	Effect of pH on the absorbance of the complexes of morin with erbium (III) and europium (III) in 50-50 DW	23
6.	Effect of pH on the absorbance of the complexes of morin with dysprosium (III) and holmium (III) in 50-50 DW	24
7.	Effect of pH on the absorbance of the complex of morin with ytterbium (III) in 50-50 DW	25
8.	Fluorescence spectra of the complex of morin with lanthanum (III) in 50-50 DW at pH 4.96	26
9.	Fluorescence spectra of the complex of morin with gadolinium (III) in 50-50 DW at pH 4.95	27
10.	Fluorescence spectra of the complex of morin with lutetium (III) in 50-50 DW at pH 5.00	28
11.	Fluorescence spectra of the complex of morin with dysprosium (III) in 50-50 DW	29

LIST OF FIGURES - Continued

FIGURE		Page
12.	Fluorescence spectra of the complex of morin with erbium (III) in 50-50 DW	30
13.	Fluorescence spectra of the complex of morin with europium (III) in 50-50 DW	31
14.	Fluorescence spectra of the complex of morin with holmium (III) in 50-50 DW	32
15.	Fluorescence spectra of morin and the complex of morin with ytterbium (III) in 50-50 DW	33
16.	Spectrophotometric isoabsorptive point for the com- plex of morin with dysprosium (III)	34
17.	Spectrophotometric isoabsorptive point for the com- plex of morin with erbium (III)	35
18.	Spectrophotometric isoabsorptive point for the com- plex of morin with europium (III)	36
19.	Spectrophotometric isoabsorptive point for the com- plex of morin with holmium (III)	37
20.	Spectrophotometric isoabsorptive point for the complex of morin with ytterbium (III)	38
21.	Determination of composition of the dysprosium (III)- morin complex in 50-50 DW at pH 5.00 by method of continuous variations.	40
22.	Determination of composition of the erbium (III)- morin complex in 50-50 DW at pH 5.00 by method of continuous variations	41
23.	Determination of composition of the europium (III)- morin complex in 50-50 DW at pH 5.50 by method of continuous variations	42

LIST OF FIGURES

FIGURE		Page
24.	Determination of composition of the holmium (III)- morin complex in 50-50 DW at pH 5.00 by method of continuous variations	43
25,	Determination of composition of the ytterbium (III)- morin complex in 50-50 DW at pH 5.00 by method of continuous variations	44
26.	Determination of composition of the dysprosium (III)- morin complex in 50-50 DW at pH 5.00 by slope ratio method	45
27.	Determination of composition of the erbium (III)- morin complex in 50-50 DW at pH 5.00 by slope ratio method	46
28.	Determination of composition of the europium (III)- morin complex in 50-50 DW at pH 5.50 by slope ratio method	47
29.	Determination of composition of the holmium (III)- morin complex in 50-50 DW at pH 5.00 by slope ratio method	48
30.	Determination of composition of the ytterbium (III)- morin complex in 50-50 DW at pH 5.00 by slope ratio method	49

INTRODUCTION

The analytical chemistry of the lanthanum series elements began in 1794 when Gadolin (26) examined the mineral which is now known as gadolinite. Since then the analytical chemistry of the lanthanum series elements has developed at a rate closely associated with the general interest in the lanthanum series elements.

Before 1945, the lanthanum series elements were frequently determined as a group with a nonselective precipitant. The oxalate method was most frequently used, and the most extensively studied. The lanthanum series elements were precipitated as their oxalates with oxalic acid (20), ammonium oxalate (11), dimethyl oxalate (118), and diethyl oxalate (33). Occasionally, the lanthanum series elements were precipitated as fluorides or hydrous oxides.

Cerium (IV) was first used as an oxidizing agent in titrimetric analysis in 1861 (52), but it was not until 1928 that Willard and Young (119) and Furman (25) established cerium as a versatile oxidizing agent. Cerium can be determined by oxidizing to cerium (IV) with peroxydisulfuric acid in the persence of silver ion, adding an excess of iron (II), and titrating the excess iron (II) with standard cerium (IV) sulfate solution. Europium can be determined volumetrically after reduction to europium (II), collecting in an excess of iron (III) and titrating the iron (II) with standard permanganate (23). This method is applicable only to materials containing relatively high percentages of europium. Ytterbium can also be determined in this manner.

Nonselective titrimetric methods have been used to determine the lanthanum series elements as a group. Ethylenediaminetetraacetic acid (EDTA) is most frequently used. Several indicators have been used for this method (7, 10, 12, 21, 24, 28, 43, 54, 55, 92, 99). Complexone III (49, 68, 69) and Trilon B (48, 50, 64, 101) are also frequently used.

Activation analysis was first employed by Hevesy and Levi (38), Seaborg and Livingwood (87), and Grinberg (30). The first work

in this field made use of the strong activities of dysprosium and europium induced by slow neutron capture. Procedures for the determination of small or trace amounts of lanthanum series elements have been developed (36,67,121,122). However, radioassays are subject to considerable variation in precision and their accuracy has never equalled that of the best analytical methods.

The lanthanum series elements' fluorescence spectra have been known since the early 1930's, but their analytical applications have not been extensive because the fluorescence spectra are weak and the best wavelength for excitation radiation is below 250 m μ . In qualitative detection tests, only lanthanum (III), gadolinium (III), and lutetium (III) formed fluorescent complexes with morin (2', 4', 3, 5, 7pentahydroxyflavone) (70). The other lanthanide (III)-morin complexes did not fluoresce. This is due to internal quenching caused by intramolecular energy transfer.

X-ray fluorescence spectra are strikingly simple compared to the absorption spectra, but the method suffers from the basic experimental difficulty of overlap of absorption edges with fluorescent spectral lines. Recently, this method was used to determine the lanthanum series elements over a wide range of concentrations (76). The lanthanum series elements can be determined as impurities in other highly purified lanthanum series elements, but adequate resolution requires a loss of spectral intensity.

Theoretically, emission spectroscopy can be used to determine all of the lanthanum series elements, but many experimental difficulties exist. Lanthanum series element spectra possess thousands of lines of uniform intensity which lack the characteristically intense lines found in emission spectra of other elements. However, using the most persistent lines, spectrography presents the simplest technique for the determination of trace quantities of the lanthanum series elements.

Using 10 mg. samples, Waring and Annel (106) have shown that the sensitivity of this method varies from 0.1 percent for cerium and samarium to 0.0001 percent for ytterbium. By employing an internal standard, Fassel et al. (15-19, 46, 47) have been able to determine major constituents in lanthanum series element matrices with an accuracy of 3-4 percent. Ko (45) developed two spectrochemical procedures for determining lanthanum series elements. Radwan et al. (73-75) have used spectrographic procedures to determine trace amounts of lanthanum series elements.

There are two methods of spectrophotometric analysis for the lanthanum series elements. The first method utilizes the band absorption spectra of the colored ions. The absorption spectra of aqueous solutions of the lanthanum series elements in the ultraviolet, visible, and infrared regions are very complex. The bands are narrow and can be attributed to pure electronic transitions involving the 4f subshell. The spectra of the lanthanide (III) perchlorates (2, 59, 65, 66, 85, 96, 97), chlorides (27, 40, 59, 65, 89, 98, 117), nitrates (59, 60, 79) and acetates (59) are of interest to the analytical chemist.

Analysis of the lanthanum series elements by absorptiometry was first proposed by Rodden (78,79), who obtained transmittanceconcentration curves for dysprosium, holmium, thullium, and ytterbium, employing the absorption bands at 910, 643, 521, 684 and 950 mµ. respectively. Praseodymium, neodymium and samarium can be determined using the 446, 798 and 402 mµ.absorption bands, respectively. Terbium can be determined using the 219 mµ.absorption band (65). The molar absorptivities of the lanthanide (III) ions are low, ranging approximately from one to ten (103). Thus the absorption bands are used for determining major constituents.

The second method utilizes the formation of intensely absorbing complexes. The formation of lanthanide (III) complexes in solution

leads to variation in the structure of the ligand absorption spectra. Moeller and Brantley (60) observed enhancement of absorption by chelate formation in their study of the absorption spectrum of neodymium with EDTA.

Several chromophoric agents are available for the spectrophotometric determination of the lanthanum series elements. The complexes which are formed generally absorb light at different wavelengths than the original dye. The lanthanum series elements have been determined using arsenazo (2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-benzenearsonic acid (8, 24, 41, 49, 51, 53, 62, 63, 83, 84). The lanthanum series elements have also been determined using Xylenol Orange (71, 90, 102), Alizarin Red S (77), sulfosalicylic acid (39), aurin tricarboxylic acid (39), napthazarin (61), and Haematoxylin (oxidized) (81). Morin has been used for spectrophotometric and spectrofluorometric determination of the lanthanum series elements and thorium (22, 56, 57, 107).

It is the purpose of this investigation to extend the studies in complexation reactions between morin and lanthanide (III) ions in 50-50 dioxane-water begun by Fleck (22) and Weiler (107). A study was undertaken to establish light absorption and fluorescence characteristics of the complexes formed between morin and europium, dysprosium, holmium, erbium and ytterbium. HISTORICAL

Several books which describe fluorescence phenomena have been published. Pringsheim discussed the theoretical aspects of fluorescence, including a chapter on the fluorescence of the lanthanum series elements (72), fluorescence theory is discussed by Bowen and Wokes (6) and by Bowen (5). In addition, C. E. White reviews the organic and inorganic applications of fluorometric analysis in "Analytical Chemistry" (109-116). Approximately 1000 references are cited in these review articles.

Morin has been tested as a reagent for the fluorometric analysis or detection of a large number of metals (1, 9, 29, 58, 70, 80, 82, 91, 95, 108).

Milkey and Fletcher (56, 57) conducted an investigation of the thorium (IV)-morin complex in slightly acidic ethanol-water mixtures. This investigation and the work of Fleck (22) and Weiler (107) was used as a pattern for this work.

Studies of the absorption of visible and ultraviolet radiation have long been used to obtain information about equilibria in solution. Early work in the visible region involved measuring the absorbance by subjective matching of light intensities, but, in 1924, von Halbin and Ebert (34) reported the determination of the dissociation constant of picric acid using a photoelectric colorimeter. The first study of equilibria based on ultraviolet absorption appears to be Stenstrom and Goldsmith's work on the dissociation of tyrosine in 1926 (94).

A number of methods still widely used to determine the formulae and stability constants of complexes were originally designed for the case in which only one complex is formed. The method of continuous variations was first applied to the formation of complexes in solution by Job (42), and was used by Denison (13, 14) in the study of liquid mixtures. Vosburg and Cooper (104) and Katzin and Geber (44) have

extended Job's treatment to systems in which two or more complexes are formed.

Bent and French (3) determined the structure and dissociation constant of ferric thiocyanate by varying the concentration of thiocyanate with a constant concentration of iron and varying the concentration of iron with a constant concentration of thiocyanate. The stability constant is obtained by analyzing the interrelationship between the logarithm of the absorbance and the logarithm of the total thiocyanate ion concentration.

The molar-ratio method of Yoe and Jones (120) is applicable to very slightly dissociated complexes. By plotting the absorbance as a function of the ratio of total concentration of anion to cation, a break in the curve is obtained at the anion/cation stoichiometric ratio.

Several workers have developed methods of determining the stability constants which employ equimolar solutions. Hagenmuller (31, 32) developed a method using equimolar solutions which is applicable only to 1:1 complexes. The method of Betts and Michels (4) is similar to Hagenmuller's, but employs non-equimolar solutions. Shaeppi and Treadwell (88) have also developed a method which employs equimolar solutions. Schwarzenbach (86) extended this method for the special case in which a 1:1 complex is formed.

EXPERIMENTAL

INSTRUMENTATION

The spectrofluorometer used in this work is a modification by Fleck (22) of the instrument constructed by Thommes (100). Figure 1 shows a block diagram of the modified instrument and the excitation and fluorescent emission radiation light paths. The components are listed here:

- The ultraviolat source is a Hanovia S-H high pressure mercury arc lamp powered by a Hanovia 110/120 constant voltage transformer. The mercury lines which were used are the 365, 405 and 436 mµ lines.
- The ultraviolet monochromator is a Bausch and Lomb model 33-86-40 grating monochromator, which is connected to the cell compartment with a light-tight 0-ring gasket.
- 3. Two clear window silica cells 10 x 20 x 50 mm., purchased from the Farrand Optical Company, were used. These cells are transparent to the above listed excitation radiation. The cells were reproducibly positioned in the cell compartment by means of a 10 x 20 mm. holder situated so that the ultraviolet beam struck the 20 mm. side.
- 4. A Beckman DU with photomultiplier attachment powered by an AC power source was used. The instrument was slightly modified as indicated in Figure 1, so that the fluorescent light entered from the position that the photomultiplier tube usually occupies and was measured by a photomultiplier tube at the position usually occupied by the lamp housing. The light-tight cell compartment was equipped with a quartz cylindrical converging lens to produce a parallel beam of ultraviolet light focused on the center of the sample cell.



Figure 1. Block Diagram of Spectrofluorometer.

The Beckman Models DU, DK-2, and DB spectrophotometers were used for the absorption measurements. The Model DU was used for the single wavelength measurements required for the stability and complex composition studies. A matched pair of 0.999 cm. silica cells was used for these measurements.

A Sargent constant temperature bath employing a Princo-Magna-Set mercury temperature control was used to maintain the temperature of solutions at 25.0 \pm 0.02[°].

A Beckman Model G pH meter equipped with a glass-saturated calomel microelectrode pair was used in all pH measurements. The instrument was calibrated with a Beckman pH 4 buffer.

REAGENTS

Ammonium Hydroxide

Mallinckrodt Chemical Works, Analytical Reagent Grade, distilled and stored in a polyethylene bottle equipped with an ascarite protection bulb.

Dichlorofluorescein

Eastman Kodak White Label.

Dioxane

Baker and Adamson's Commercial Grade.

Dysprosium, Erbium, Gadolinium, Holmium, Lutetium and Ytterbium Sesquioxides

Michigan Chemical Corporation, St. Louis, Michigan. Labeled 99.9% pure.

Europium Sesquioxide

Michigan Chemical Corporation, St. Louis, Michigan. Labeled 99.8% pure.

Hydrochloric Acid

Baker's Reagent Grade.

Lanthanum Sesquioxide

Optical Grade, Heavy Minerals Company, Chattanooga, Tennessee,

Morin Dihydrate

Dr. Theodor Schuchardt, München, Germany.

Perchloric Acid

Baker's Analyzed Reagent Grade, 70-72%.

Sodium Perchlorate

Baker's Analytical Reagent, recrystallized.

Water

Distilled from potassium permanganate.

PREPARATION OF REAGENT SOLUTIONS

Ammonium Hydroxide

The ammonium hydroxide used for pH adjustment was about 0.1 M and was prepared from the distilled material.

Dichlorofluorescein

A 0.4 γ per ml. solution in 4% ethanol was prepared by dilution of a stock solution prepared by dissolving a weighed quantity of the reagent in 95% ethanol.

Dioxane

A modification of the procedure of Hess and Frahm (37) was used to purify commercial grade dioxane. A mixture of 4 l. of dioxane, 400 ml. of distilled water, and 54 ml. of concentrated hydrochloric acid was refluxed for 12 hours, during which time a slow stream of nitrogen was bubbled through the solution to sweep out aldehydes. The solution was cooled, and potassium hydroxide pellets added slowly with mixing until the solution became saturated and a second layer formed. The dioxane was decanted and treated with additional potassium hydroxide. The partially dried dioxane was then decanted into a screw-cap bottle containing anhydrous calcium chloride. After standing at least overnight, the dioxane was filtered into a 5 liter round-bottom flask, refluxed over calcium hydride for 12 hours and distilled. A 50 ml, forecut and about 300 ml. heel were discarded. The product, distilled at $100 \pm 0.5^{\circ}$, was stored in an amber-colored screw-capped bottle.

Lanthanide Oxides

Portions of the various oxides were ignited to constant weight in platinum crucibles at $750 \pm 25^{\circ}$. The ignited oxides were dissolved in a measured amount of perchloric acid so that the final solution had a 0.2 M. perchlorate ion concentration and a 1.0 mg. per ml. cation concentration. Since the claimed purity of these reagents was high, the solutions were not standardized. Aliquots of these solutions were taken for the preparation of the working solutions of 0.1 mg. of lanthanide (III) ion per ml.

Morin

A weighed portion of morin dihydrate reagent was dissolved in purified dioxane to produce a solution of 1.655×10^{-3} M.

Perchloric Acid

The perchloric acid used for pH adjustment was about 0.1 M and was prepared by dilution of the reagent acid.

EXPERIMENTAL PROCEDURES

All experimental work was carried out at $25 \pm 1^{\circ}$. All solutions were placed in a constant temperature bath maintained at $25.0 \pm 0.02^{\circ}$ for a minimum of one-half hour before making measurements.

Method of Sample Preparation

The desired lanthanide perchlorate working solution was measured quantitatively into a 30 ml. beaker and the morin solution quantitatively added to it. Pure dioxane was added to it to give a total dioxane volume of 12.5 ml. Distilled water was added to give a total volume of 21-22 ml. The pH of the solution was adjusted with dilute ammonium hydroxide and/or perchloric acid until the desired pH was approximated. The resulting solution was transferred to a 25 ml. volumetric flask¹ and the sample was diluted to the mark. Exact pH was measured after the solution had been equilibrated for one hour in the thermostated water bath.

Instrumental Measurements

Spectrofluorometric Measurements

All spectrofluorometric measurements were made with the spectrofluorometer described in the instrumentation section and shown in Figure 1. The Beckman DU, its AC power supply and the mercury arc lamp were allowed to warm up for at least thirty minutes to insure instrumental stability. The photomultiplier sensitivity control knob was set to the "full" position and the Beckman DU knob set three turns

¹All work in this investigation was carried out using 25 ml. volumetric flasks unless otherwise stated.

from its clockwise limit. The monochromator entrance and exit slits were set to 1.0 and 0.5 mm. respectively, and the Beckman DU slit adjusted to approximately 1.0 mm.

To standardize the instrument, the ultraviolet monochromator was adjusted to pass the 365 m μ mercury line. The Beckman DU selector switch is set to the 0.1 position, and its monochromator set for 530 m μ . The 0.4 γ per ml. dichlorofluorescein solution was placed in the cell, the shutter opened and the instrument balanced by adjustment of the Beckman entrance slit so that a "%T" reading at 50 was obtained.

After standardization, the Bausch and Lomb, and the Beckman monochromators were adjusted to the desired wavelength and measurement of the samples' fluorescence intensities recorded as "%T" readings.

Nature of the Complex

Isoabsorptive Point

In order to determine the number of complexes which might be formed, and to determine whether the reaction is stoichiometric, a series of solutions containing 400 γ of morin and amounts of lanthanide (III) varying between 0.0 and 0.8 mg. per 25 ml. as indicated were prepared and adjusted to the desired pH. The absorbances of these solutions were recorded from 340 to 660 mµ. using the Beckman DK-2 or DB.

Method of Continuous Variations

Job's method of continuous variations (42) was employed to determine the empirical formula of the complex formed. The absorbances for dysprosium (III) and erbium (III) systems were measured at 356, 390 and 414 mµ., for holmium (III) and ytterbium (III) systems at 356, 390 and 419 mµ., and for the europium (III) system at 356, 390 and 408 mµ.

Slope-Ratio Method

In order to confirm the composition of the complex, the sloperatio method of Harvey and Manning (35) was employed. Twelve solutions containing lanthanide (III) ranging in concentration from approximately 0.7×10^{-6} M. to 12.1×10^{-6} M. in the presence of a large excess of morin, 1.32×10^{-4} M., were prepared. The absorbances of these solutions were measured at the desired wavelength and plotted against concentration of lanthanide (III) ions, and the slope of the line determined. Twelve solutions containing morin in the concentration range of approximately 0.6×10^{-5} M. to 7.0×10^{-5} M. in the presence of a large excess of lanthanide (III) ion were also prepared. The absorbances were plotted against concentrations of morin and the slope of the line determined.

DISCUSSION OF RESULTS

General

Morin (2', 4', 3, 5, 7-pentahydroxyflavone) forms complexes with dysprosium, erbium, europium, holmium and ytterbium. The absorption spectra of morin and the complexes are shown in Figures 2-4. The reagent has an absorption peak at 356 mµ., and 408, 414, and 419 mµ. are the absorption peak wavelengths for europium, dysprosium and erbium, holmium and ytterbium complexes, respectively.

Figures 11-15 show that the complexes do not fluoresce significantly when exposed to ultraviolet radiation. Figures 8-10 show that the complexes of lanthanum, gadolinium and lutetium flouresce under these conditions. These results confirm the observations of Pollard et al. (70). It should be noted that morin also fluoresces to a slight extent at pH 5.00.

Parameters Effecting the Absorbance

Effect of pH of the Solution

Figures 5-7 show the effect that change in pH has upon the absorbance of the complex. The absorption maximum of the complex shifts to higher wavelengths with increase in pH.

Effect of Ionic Strength

The effect of ionic strength was studied using sodium perchlorate. The absorption spectra, not shown, indicate that the addition of sodium perchlorate to the lanthanide (III)-morin complex has no effect upon the absorbance of the solution.

Nature of the Complex

Isoabsorptive Point

Figures 16-20 show spectrophotometric isoabsorptive points for the five lanthanide (III) complexes. The isoabsorptive point of the



Figure 2. Absorption Spectra of Morin and the Complexes of Morin with Dysprosium (III) and Erbium (III) in 50-50 DW at pH 5,00.



Figure 3. Absorption Spectra of Morin and the Complexes of Morin with Holmium (III) and Ytterbium (III) in 50-50 SW at pH 5.00.

1.0 400 γ Morin О 0.9 Europium (III)-Morin Complex (100 γ Eu(III)) 0.8 0.7 0.6 Absorbance **7.0** 0.3 0.2 0.1 350 360 370 380 390 400 410 420 430 Wavelength in $M\mu$.

Figure 4. Absorption Spectra of Morin and the Complex of Morin with Europium (III) in 50-50 DW at pH 5.50.








































Figure 15. Fluorescence Spectra of Morin and the Complex of Morin with Ytterbium (III) in 50-50 DW.



Figure 16. Spectrophotometric Isoabsorptive Point for the Complex of Morin with Dysprosium (III).



Figure 17. Spectrophotometric Isoabsorptive Point for the Complex of Morin with Erbium (III).







europium-morin complex was determined at pH 5.50, while the other lanthanide (III) complexes were studied at pH 5.00. The formation of an isoabsorptive point suggests the occurrence of a single reaction (56) between the lanthanide (III) ion and morin.

Method of Continuous Variations

The empirical formula of the complex was determined by employing Job's method of continuous variations. The total molar concentrations of lanthanide (III) ion and morin were maintained constant for a series of solutions, while the individual concentrations of lanthanide (III) ion and morin were varied. The mole fraction of lanthanide (III) ion was plotted against Y, the corrected absorbance which is due only to the complex.

Job (42) and Vosburgh and Cooper (105) have shown that the value of Y at each wavelength is a maximum where the greatest amount of complex is formed. Figures 21-25 show the results obtained when Y for the complex is plotted against the mole fraction of lanthanide (III) ion. The maximum or minimum value of Y appears at a ratio of one mole of lanthanide (III) ion to two moles of morin, indicating a general formula for the complex of RM_2^+ .

Slope Ratio Method

The composition of the complexes was also determined by the slope ratio method of Harvey and Manning (35). Figures 26-30 show the absorbance at the maximum for the complex plotted against the moles of morin per liter, curve 1, and the moles of lanthanide (III) ion per liter, curve 2, for the slope ratio method. The slope of curve 1 represents the change in absorbance per mole of morin, and curve 2 represents the change in absorbance per mole of lanthanide (III) ion.

































ļ







The data obtained, as well as the slope ratios, are summarized in the Appendix (Tables A-VI-A-X). These data confirm the results obtained in the continuous variations study, namely that the general formula of the complex is RM_2^+ .

Equilibrium Ratios of the Complexes

The technique used by Milkey and Fletcher (56) in their investigation of the thorium (IV)-morin complex was employed to estimate the equilibrium ratio of the various lanthanide (III) ion-morin complexes. The following information was obtained to perform the calculations of the equilibrium ratios of the complexes under the conditions of the investigation.

Absorptivity of Morin

Solutions containing morin in the concentration range of approximately 0.1 x 10^{-4} M. to 2.5 x 10^{-4} M., and no lanthanide (III) ions were prepared. The solutions were adjusted to the desired pH and the absorbance, A, was measured, from which the molar absorptivity was calculated. The molar absorptivity of morin at pH 5.50 and 408 mµ. is 2.52 x 10^3 L/mole cm. at pH 5.00 and 414 mµ. is 1.44 x 10^3 L/mole cm., and at pH 5.00 and 419 mµ. is 1.31×10^3 L/mole cm.

Absorptivity of the Lanthanide (III)-Morin Complex

The molar absorptivity of the various complexes was calculated from the slope ratio data obtained in the presence of a large excess of the lanthanide (III) ion. The large excess of lanthanide (III) ion insured the complete reaction of all of the morin added to form the complex. On the basis of the assumption that for each two moles of morin added, one mole of complex is formed, the molar absorptivity of the complex will be equal to an absorbance value divided by one-half of the corresponding morin concentration.

Concentration of the Components in Solution After Complex Formation

The calculation, as employed by Milkey and Fletcher (56) to determine the concentration of the components in a solution of the complex, was performed with the data obtained in the continuous variations investigation.

In the lanthanide (III) morin system only morin and the complex absorb light.

- If: X = moles of complex per liter
 - (MH) = total moles of morin added per liter
 - $(R^{+++}) = total moles of lanthanide (III) per liter$
 - Y = moles of uncombined morin per liter
 - Z = moles of uncombined lanthanide (III) ion per liter
 - A = absorbance at desired wavelength of solutions containing the complex
 - b = path length in cm. (0.999 cm.)
 - a_{MH} = molar absorptivity of morin at desired pH and wavelength
 - $a_{RM_2}^{+}$ = molar absorptivity of the complex at desired pH and wavelength

then

$$A = a_{MH} [(MH) - 2(X)] + a_{RM_2}^{+}(X)$$

Solving for X:

$$X = \frac{A - a_{MH}(MH)}{a_{RM_2}^+ - 2(a_{MH})}$$

In addition, the concentration of uncombined morin and lanthanide (III) ion remaining in solution may be calculated as follows:

$$Y = (MH) - 2(X)$$

and $Z = (R^{+++}) - X$

Calculation of the Equilibrium Ratio

Once the concentrations of the components present in solution have been calculated, the equilibrium ratio, K'_{eq} for the reaction,

$$R^{+++} + 2 MH = R(M)_2^+ + 2 H^+$$

and be evaluated by substitution of the appropriate values into the expression

$$K'_{eq} = \frac{R(M)_{2}^{+}(H^{+})^{2}}{(R^{+++})(MH)^{2}}$$

where

These data are shown in the Appendix (Tables A-I - A-V). The average values for K' are 15.1, 19.4, 20.9, 24.6 and 31.5 for eq europium, dysprosium, holmium, erbium and ytterbium, respectively. These values are consistent with the values obtained by Fleck (22) for lanthanum and by Weiler (107) for gadolinium and lutetium.

SUMMARY AND CONCLUSIONS

A spectrophotometric and spectrofluorometric investigation of the complexes which form when dysprosium (III), erbium (III), europium (III), holmium (III) or ytterbium (III) is added to 50-50 DW solutions of morin was completed.

The absorption band peak of morin occurs at 356 m μ ., while the complex absorption band peaks for europium, dysprosium and erbium, holmium and ytterbium occur at 408, 414 and 419 m μ ., respectively.

The complexes fluoresce only slightly more than morin when exposed to 365, 405 or 436 m μ . radiation. The complexes of lanthanum, gadolinium and lutetium fluoresce under the same conditions.

The pH of the solution affects the absorbance of the complexes. The absorbance maximum for the europium complex occurs at pH 5.50, and the absorbance maxima for the dysprosium, erbium, holmium and ytterbium complexes occur at pH 5.00. The absorption maxima shift slightly to longer wavelengths with increasing pH.

The ionic strength effect by sodium perchlorate, up to 0.1 M., was negligible.

In the absorption spectra of each of the complexes, a single isoabsorptive point exists. The isoabsorptive point for the europiummorin system occurs at 376 mµ., the erbium-morin and ytterbiummorin systems at 380 mµ., the dysprosium-morin system at 382 mµ., and the holmium-morin system at 388 mµ. The existence of an isoabsorptive point suggests that a single complex is formed.

Job's method of continuous variations (42) and Harvey and Manning's slope ratio method (35) were employed to determine the empirical formula of the complex. These studies indicate that a 1:2 complex, lanthanide (III):morin, is formed.

An equilibrium ratio, K'_{eq} , for each of the complexes was evaluated. The K'_{eq} values for the europium, dysprosium, holmium, erbium 15.1, change tration 1.32 x

•

į.

erbium and ytterbium complexes with morin in 50-50 DW at 25° are 15.1, 19.4, 20.9, 24.6 and 31.5, respectively.

The absorbances for the complexes change linearly with change in lanthanide (III) concentration over the approximate concentration ranges, 0 to 1.4×10^{-5} M., in the presence of excess morin, 1.32×10^{-4} M.

LITERATURE CITED

- Bailar, J. C. Jr., "The Chemistry of Coordination Compounds," Reinhold, New York, New York, (1956).
- Banks, C. V. and Klingman, D. W., Anal. Chim. Acta., <u>15</u>, 356 (1956).
- 3. Bent, H. E., and French, C. L., J. Am. Chem. Soc., <u>63</u>, 568 (1941).
- 4. Betts, R. H., and Michels, R. K., J. Chem. Soc., <u>1949</u>, 286.
- 5. Bowen, E. J., "The Chemical Aspects of Light," 2nd Ed., Oxford Press, London, 1946.
- 6. Bowen, E. J., and Wokes, F., "Fluorescence of Solutions," Longmans, Green and Co., New York, 1953.
- 7. Bril, K. Y., Holzek, S., and Rethy, B., Anal. Chem., <u>31</u>, 1353 (1959).
- Budeninsky, B., Collection Czech. Chem. Commun., <u>28</u>, 2902 (1963); C. A., <u>60</u>, 3478d (1964).
- 9. Charlot, G., Anal. Chim. Acta., 1, 218 (1947).
- 10. Cheng, K. L., Chemist Analyst, 47, 93 (1958).
- 11. Clinch, J., and Simpson, E. A., Analyst, 82, 258 (1957).
- Crouch, E. A. C., and Swainbank, I. G., United Kingdom Atomic Energy Authority, Rept. AERE-C/R-2843 (Feb., 1959).
- 13. Denison, R. B., Trans. Faraday Soc., 8, 20 (1912).
- 14. Denison, R. B., Trans. Faraday Soc., 8, 35 (1912).
- 15, Fassel, V. A., Iowa State J. Sci., 22, 21 (1947).
- 16. Fassel, V. A., J. Opt. Soc. Amer., 39, 43, 187 (1949).
- 17. Fassel, V. A., Cook, H. D., Krotz, L. C., and Kehres, P. W., Spectrochim. Acta., 5, 201 (1952).

- Fassel, V. A., Quinney, B., Krotz, L. C., and Lentz, C. F., Anal. Chem., <u>27</u>, 1010 (1955).
- 19. Fassel, V. A., and Wilhelm, H. A., J. Opt. Soc. Amer., <u>38</u>, 518 (1948).
- 20. Fitch, F. T., and Russell, D. S., Anal. Chem., 23, 1469 (1951).
- 21. Flaschka, H., Mikrochim. Acta., 1955, 55.
- 22. Fleck, L. L., Ph. D. Thesis, Michigan State University, East Lansing, Michigan (1961).
- 23. Foster, D. C., and Kremers, H. E., Anal. Chem., <u>25</u>, 1921 (1953).
- 24. Fritz, J. S., Abbink, J. E., and Payne, M. A., Anal. Chem., <u>33</u>, 1381 (1961).
- 25. Furman, H. H., J. Am. Chem. Soc., 50, 755 (1928).
- 26. Gadolin, J., Vetenskapsakad. Handl., 15, 137 (1794).
- 27. Ganopol'skii, V. I., Ganopol'skaya, T. A., and Barkovskii, V. F.,
 Zh. Analit. Khim., <u>18</u>, 729 (1963); C. A., <u>59</u>, 8116c (1963).
- 28. Gimesi, O., Rady, G., and Erdey, L., Periodica Polytech., <u>6</u>, No. 1, 15 (1962); C. A., <u>58</u>, 6167b (1963).
- 29. Goto, H., J. Chem. Soc. Japan, <u>60</u>, 937 (1939); C. A., <u>34</u>, 4355.
- 30. Grinberg, A. A., Achievements in Chemistry, 9, 771 (1940).
- 31. Hagenmuller, P., Ann. Chim. Paris, 6, 5 (1951).
- 32. Hagenmuller, P., Compt. Rend., 230, 2190 (1950).
- 33. Hagiwara, Z., Technol. Rept. Tohoku Univ., 20, 77 (1955).
- 34. Halban, H. von, and Ebert, L., Z. physik. Chem. (Leipzig), <u>112</u> 359 (1924).
- 35. Harvey, A. E., Jr., and Manning, D. L., J. Am. Chem. Soc., <u>72</u>, 4488 (1950).
| 36 |
|----|
| 37 |
| 38 |
| 39 |
| 40 |
| 41 |
| 47 |
| 43 |
| 44 |
| 45 |
| 46 |
| |
| 47 |
| 48 |
| 49 |
| 50 |
| |
| |

- 36. Haskin, L., and Gehl, M. A., J. Geophys. Research, <u>67</u>, 2537-41 (June, 1962); N.S.A., 16, 20841 (1962).
- 37. Hess, K., and Frahm, H., Ber., 71, 2627 (1938).
- Hevesy, G. von, and Levi, H., Kgl. Danske Videnske Selskab. Nat. Fys. Medd., 14, N.S.A. (1936).
- 39. Holleck, L., Eckhardt, D., and Hartinger, L., Zh. Analit. Chem., <u>146</u>, 103 (1955).
- 40. Holleck, L., and Hartenger, L., Angew. Chem., 67, 648 (1955).
- 41. Iordanov, M., and Daiev, K., Izv. Inst. po Obshcha Neorg. Khim. Org. Khim., Bulgar Akad. Nauk, 9, 19 (1962); C. A., 59, 9298g (1963).
- 42. Job, P., Ann. Chim., 9, 113 (1928).
- 43. Katsumata, S., Bunseki Kagaku, <u>10</u>, 1259 (1961); C. A., <u>58</u>, 6173h (1963).
- 44. Katzin, L. I., and Gebert, E., J. Am. Chem. Soc., 72, 5455 (1950).
- 45. Ko, R., U. S. At. Energy Comm. HW-71517, 8pp., (1962); N.S.A., <u>16</u>, 27001 (1962).
- 46. Kniseley, R. N., Fassel, V. A., Quinney, B. B., Tremmer, C., Gordon, W. A., and Hayles, W. J., Spectrochim. Acta., <u>12</u>, 332 (1958).
- 47. Kniseley, R. N., Fassel, V. A., Tabeling, R. W., Hurd, B. G., and Quinney, B. B., Spectrochim. Acta., 13, 300 (1959).
- Kugai, L. N., Tr. Seminara po Zharostoikim Materialam, Akad. Nauk Urr. SSR., Inst. Mettalokeram. i Spets. Splavov, Kiev, 1960; C. A., <u>56</u>, 12300b (1962).
- 49. Kugai, L. N., and Nazarchuk, T. N., Zh. Analit. Khim., <u>16</u>, 205 (1961); C. A., <u>56</u>, 12299g (1962).
- Kuteinikov, A. F., and Brodskaya, V. M., (All-Union Scientific Research Institute of Mineral Resources, USSR), Zavodskaya Lab., <u>28</u>, 792 (1962); N.S.A., <u>16</u>, 26940 (1962).

- 51. Kuznetsov, V. I., Zh. Analit. Khim., 7, 226 (1952).
- 52. Lange, L. T., J. prakt. Chem., (1) 82, 129 (1861).
- 53. Lorenzina, L., Stoppa, C., and Barbieri, W., Met. Ital., <u>54</u>, 380 (1962); C. A., <u>58</u>, 1900e (1963).
- 54. Lyle, S. J., and Rahman, M. M., Talanta, 10, 1177 (1963).
- 55. Lyle, S. J., and Rahman, M. M., Talanta, 10, 1183 (1963).
- 56. Milkey, R. G., and Fletcher, M. H., Anal. Chem., 28, 1403 (1956).
- 57. Milkey, R. G., and Fletcher, M. H., J. Am. Chem. Soc., <u>79</u>, 5425 (1957).
- 58. Minczewski, J., and Rutkowski, W., Chem. Anal. (Warsaw), 7, 1107 (1962); C. A. 58, 13116d (1963).
- 59. Moeller, T., and Brantley, J. C., Anal. Chem., 22, 433 (1950).
- 60. Moeller, T., and Brantley, J. C., J. Am. Chem. Soc., <u>72</u>, 5447 (1950).
- 61. Moeller, T., and Telotzky, M., J. Am. Chem, Soc., 77, 2649 (1955).
- 62. Onishi, H., and Banks, C. V., Talanta, <u>10</u>, 399 (1963).
- Onishi, H., Nagai, H., and Toita, Y., Anal. Chim. Acta., <u>26</u>, 528 (1962); C. A., <u>57</u>, 6602d (1962).
- 64. Onosova, S. P., Zavodsk. Lab., <u>28</u>, 271 (1962); C. A., <u>57</u>, 2836f (1962).
- 65. Onstott, E. I. and Brown, C. J., Anal. Chem., 30, 172 (1958).
- Palmino, J. V., Castillo, F. de La Cruz, and Cellini, R. F., Anales. Real Soc. Espan. Fis. Quim. (Madris) Ser. B., <u>59</u>, 303 (1963); C. A., <u>59</u>, 10758g (1963).
- 67. Pappas, A. C., Alstad, J., and Lunde, G., Radiochim. Acta, <u>1</u>, 109 (1963); N.S.A., <u>17</u>, 28812 (1963).

- Peshkova, V. M., Gromova, M. I., and Aleksandrova, N. N., Zh. Analit. Khim., 17, 218 (1962); N.S.A., 16, 18842 (1962).
- Peshkova, V. M., Gromova, M. I., Efimov, I. P., and Isachenko, A. V., Vestnik. Moskov. Univ., Khim., Ser. II 16, No. 4, 59 (1961); C. A., 56, 7980a (1962).
- 70. Pollard, F. H., McOmie, J. F. W., and Stevens, H. M., J. Chem. Soc., 4730 (1952).
- 71. Prajsnak, D., Chem. Anal. (Warsaw), <u>8</u>, 71 (1963); C. A., <u>58</u>, 13114c (1963).
- 72. Pringsheim, P., "Fluorescence and Phosphorescence," Interscience, New York, 1949.
- 73. Radwan, Z., Strzyzewska, B., and Minczewski, J., Appl. Spectry., <u>17</u>, No. 1, 1 (1963); C. A., <u>58</u>, 11948e (1963).
- 74. Radwan, Z., Strzyzewska, B., and Minczewski, J., Appl. Spectry., 17, No. 3, 60 (1963); C. A., 59, 4540c (1963).
- 75. Radwan, Z., Strzyzewska, B., and Minczewski, J., Chem. Anal. (Warsaw), <u>6</u>, 959 (1961); C. A., <u>56</u>, 13535a (1962).
- 76. Renev, V. K., and Ganopol'skii, V. I., Zavodsk. Lab., <u>29</u>, 1076 (1963); C. A., <u>60</u>, 17g (1964).
- 77. Rinehart, R. W., Anal. Chem., 26, 1820 (1954).
- 78. Rodden, C. J., J. Research Natl. Bur, Standards, 26, 557 (1941).
- 79. Rodden, C. J., J. Research Natl. Bur. Standards, 28, 265 (1941).
- 80. Rutkowski, W., Chem. Anal. (Warsaw), <u>8</u>, 389 (1963); C. A., <u>60</u>, 3474g (1964).
- 81. Sarma, T. P., and Rao, B. S. V. R., J. Sci. Ind. Research (India), <u>14B</u>, 450 (1964).
- Savokovskaya, N. A., Voskresenskaya, M. M., and Mel'nikova, T. A., Nauchn. Soobschch, Inst. Gorn. Delaim. A. A. Skochinskogo, <u>13</u>, 30 (1962); C. A., <u>58</u>, 11941h (1963).

- 83. Savvin, S. B., Zavodsk. Lab. 29, 131 (1963); C. A., 59, 3e (1963)
- 84. Savvin, S. B., and Muk, A. A., Bull. Inst. Nucl. Sci. "Boris Kidrich," (Belgrade), 12, 97 (1961); N.S.A., 16, 14653.
- Schultz, C. G., U. S. Atomic Energy Comm. TID-6423, 6 pp, (1957) (Declassified 1959).
- 86. Schwarzenbach, G., Helv. Chim. Acta, 32, 839 (1949).
- 87. Seaborg, G. T., and Livingwook, J. J., J. Am. Chem. Soc., <u>60</u>, 1784 (1938).
- 88. Shaeppi, Y., and Treadwell, W. D., Helv. Chim. Acta, 577 (1948).
- Shcherbov, D. P., Mirkin, V. A., and Klimov, V. V., Tr. Kazakhsk. Nauchn.-Issled. Inst. Mineral'n Syr'ra, <u>1960</u>, No. 3, 296; C. A., <u>57</u>, 9194h (1962).
- 90. Sheka, Z. A., and Sinyavskaya, E. I., Zh. Analit. Khim., <u>18</u>, 460 (1963); C. A., 59, 2157g (1963).
- 91. Sill, C. W., and Willis, C. P., Anal. Chem., 31, 598 (1959).
- 92. Sin, Peng-Joung, J. Chinese Chem, Soc. (Taiwan), Ser. II9, 41 (1962); C. A., 58, 2838e (1963).
- 93. Spedding, F. H., and Daane, A. H., "The Rare Earths," J. Wiley and Sons, Inc., New York, p. 611.
- 94. Stenstrom, W., and Goldsmith, N., J. Phys. Chem., <u>30</u>, 1683 (1926).
- 95. Stevens, H. M., Anal. Chim. Acta, 20, 389 (1959).
- 96. Stewart, D. C., AEC, Rept. AECD-2389 (Sept., 1948).
- 97. Stewart, D. C., AEC, Rept. ANL-5624 (Oct., 1956).
- 98. Stewart, D. C., and Kato, D., Anal. Chem., 30, 164 (1958).
- 99. Tereshin, G. S., and Tananaev, I. V., Zh. Analit. Khim., <u>17</u>, 526 (1962); C. A., <u>57</u>, 14420a (1962).

- 100. Thommes, G. A., Ph. D. Thesis, Michigan State University, East Lansing, Michigan (1956).
- 101. Tikhonov, V. N., Tr., Vses. Nauchn.-Issled. Alyumin.-Magnievyi Inst., 1961, No. 47, 145; C. A., 57, 4010i (1962).
- 102. Tonosaki, K., and Otono, M., Bull. Chem. Soc. Japan, <u>35</u>, 1683 (1962); C. A., 58, 1902e (1962).
- 103. Vickery, R. C., "Analytical Chemistry of the Rare Earths," Pergamon Press, New York (1961).
- 104. Vosburgh, W. C., and Cooper, G. R., J. Am. Chem. Soc., <u>63</u>, 437, (1941).
- 105. Vosburgh, W. C., and Cooper, G. R., J. Am. Chem. Soc., <u>72</u>, 4488 (1950).
- 106. Waring, C. L., and Annel, C. S., Anal. Chem., 25, 1174 (1953).
- 107. Weiler, J. E., M. S. Thesis, Michigan State University, East Lansing, Michigan (1961).
- 108. Welford, G., and Harvey, J., Am. Ind. Hyg. Assoc., Quart., 13, 232 (1952); N.S.A., 7, 1069 (1953).
- 109. White, C. E., Anal. Chem., 21, 104 (1949).
- 110. Ibid., 22, 69 (1950).
- 111. Ibid., 24, 85 (1952).
- 112. Ibid., 26, 129 (1954).
- 113. Ibid., 28, 621 (1956).
- 114. Ibid., 30, 729 (1958).
- 115. Ibid., 32, 47R (1960).
- 116. Ibid., 34, 81R (1962).
- 117. White, J. C., and Apple, R. F., Talanta, 2, 176 (1959).
- 118. Willard, H. H., and Gordon, L., Anal. Chem., 20, 165 (1948).

- 119. Willard, H. H., and Young, P., J. Am. Chem. Soc., <u>50</u>, 1322 (1928).
- 120. Yoe, J. H., and Jones, A. L., Ind. Eng. Chem., Anal. Ed., 16, 111 (1944).
- 121. Yoshida, H., and Takahashi, M., Bunseki Kagaku, <u>10</u>, 954 (1961); C. A., <u>58</u>, 6179g (1963).
- 122. Zamyatnina, V. N., and Chikisheva, L. A., Radiokhimiya,
 5, 294 (1963); C. A., 59, 14568f (1963).

APPENDIX

III) Morin Complex in 50-50	
Values of the Dysprosium (
K' _{eq} .,	•
Estimated Equilibrium Ratio,	DW at 25
Table A-I.	

T rial	Total Dy ⁺⁺⁺ Added M/1 x 10 ⁶	Total MH ¹ Added M/1 x 10 ⁶	H ⁺ M/1 × 10 ⁶	Z ² M/1 × 10 ⁶	Y ³ M/1 × 10 ⁶	$D_{y}(M)_{z}^{+}$ N/1 x 10 ⁶	A414	Kı eq
].	4.92	44.3	9.12	1	28.6	7.86	.341	
2.	9.84	39.4	10.7	-	17.2	11.1	.450	1 1 1
з.	12.3	36.9	10.7		12.1	12.4	.492	1 1 1 1
4.	14.8	34.4	8.91	1.1	7.0	13.7	.535	20.2
ъ.	16.0	33.2	9.12	2.1	5.4	13.9	.542	18.9
6.	17.2	32.0	10.5	3.6	4.8	13.6	.539	18.1
7.	19.7	29.5	9.55	6.5	3.1	13.2	.511	19.3
8.	24.6	24.6	9.77	13.3	2.0	11.3	.436	20.3
.6	29.5	19.7	8.91	20.4	1.5	9.08	.350	15.7*
10.	34.4	14.8	10.2	27.4	0.9	6.95	. 268	32.6*
11.	39.4	9.84	10.0	34.8	0.7	4.58	.177	28 . 5*
12.	44.3	4.92	10.5	47.0	0.2	2.34	060.	106. *

¹MH=Morin ²Z = Moles of uncombined Dysprosium (III) per liter.

³Y = Moles of uncombined Morin per liter.

⁴Absorbance values and data were obtained from solutions used in the continuous variation study. Not included in the calculation of the average value.

DW
50
50-
in
lex
dm
ပိ
rin
Mo
(111)
H
rbiı
ы a)
the
s of
lue
Va
а. С
Ki
°.
Rati
E E
riu
dili
Equ
ed H
o••••
stir 25
at E
- II.
e A
a bl
н

Trial	Total Er ⁺⁺⁺ Added M/1 x 10 ⁶	Total MH ¹ Added M/1 x 10 ⁶	H ⁺ M/1 × 10 ⁶	Z ² M/1 × 10 ⁶	Y ³ M/1 × 10 ⁶	${\rm Er}({\rm M})^{+}_{z}$ M/1 x 10 ⁶	4 A414	K' eq
	4.79	43.1	10.0	1	24.8	9.17	.370	
2.	9.58	38.3	9.33	-	15.3	11.5	.440	8 9 8
3.	12.0	35.9	9.55		11.1	12.4	.468	8 8 9 9
4.	14.4	33.5	10.0	1.1	6.9	13.3	.494	25.4
5.	15.6	32.3	10.0	2.1	5.3	13.5	.499	22.9
.9	16.8	31.1	9.55	3.2	3.9	13.6	.501	25.5
7.	19.2	28.7	10.0	6.2	2.7	13.0	.478	28.8
%	24.0	24.0	10.2	13.0	2.0	11.0	.404	22.0
9.	28.7	19.2	10.0	19.8	1.4	8.90	.327	22.9
10.	33.5	14.4	11.0	26.9	1.3	8.55	.241	17.9*
11.	38.3	9.58	9.55	33.7	.48	4.55	.167	53 . 4*
12	43.1	4.79	10.2	40.7	. 09	2.35	.086	74.6 [≸]

 $^{1}MH = Morin$

= Moles of uncombined Erbium (III) per liter

= Moles of uncombined Morin per liter ZZ²Z

⁴Absorbance values and data were obtained from solutions used in the continuous variation study. *Not included in the calculation of the average value.

•

Table A-111. Estimated Equilibrium Ratio, Kr_{eq}., Values of the Europium (111) Morin Complex in 50-50 nutrines

!

•

Estimated Equilibrium Ratio, K'_{eq.}, Values of the Europium (III) Morin Complex in 50-50 DW at 25⁰ Table A-III.

Kieq	1	1 1 1	8 1 8	15.0	13.5	15.8	15.0	16.2	4. 2 [*]	2.8 [*]	15.2	45.2 [*]	
4 A408	. 502	• 569	.589	.601	.614	.610	.577	.485	.381	. 285	.192	.097	
Eu(M) ⁺ M/1 x 10 ⁶	11.7	14.1	15.0	15.7	16.0	16.0	15.5	12.8	10.0	7.47	5.08	2.56	
Y ³ M/1 x 10 ⁶	24.0	13.9	9.5	5.9	3.6	2.2	1.2	0.7	1.1	0.9	0.3	0.1	
Z ² M/1 x 10 ⁶	5 3 9 9	1 1 1	1 1 1	0.3	1.1	2.4	5.9	13.5	21.6	28.4	37.0	44.8	
H ⁺ M/1 × 10 ⁶	3.24	3,31	3.47	3.16	3.47	3.39	2.95	2.88	3,31	2.95	3.16	2.82	
Total MH ¹ Added M/1 × 10 ⁶	47.4	42.1	39.5	36.9	35.6	34.2	31.6	26.3	21.1	15.8	10.5	5.26	
Total Eu Added M/l x 10 ⁶	5.26	10.5	13.2	15.8	17.1	18.4	21.1	26.3	31.6	36.9	41.2	47.4	
Trial	١.	2.	3.	4.	5	6.	7.	. 8	9.	10.	11.	12.	

 $^{1}MH = Morin$

= Moles of uncombined Europium (III) per liter ²2 3Ү

= Moles of uncombined Morin per liter

Absorbance values and data were obtained from solutions used in the continuous variation study. Not included in the calculation of the average value.

į

Table A. IV. Barmared Equilibrium Ratio, Rieq., Valuea of the Trainium (IID Morrin Complex in 50-50 DW at 25

Estimated Equilibrium Ratio, K'_{eq.}, Values of the Holmium (III) Morin Complex in 50-50 DW at 25⁰ Table A-IV.

Trial	Total Ho Added M/1 x 10 ⁶	Total MH ¹ Added M/1 × 10 ⁶	H ⁺ M/1 × 10 ⁶	Z ² M/1 × 10 ⁶	r^3 $M/1 \times 10^6$	Ho(M) ₂ M/1 × 10 ⁶	4 A419	K' eq.
١.	4.90	43.9	9.55	0 0 0 0	31.7	6.11	.390	
2.	9.70	39.0	10.5	8 1 8	17.2	10.9	.511	
3.	12.2	36.6	9.77	0.1	12.4	12.1	.592	75.2*
4.	14.6	34.1	10.5	1.3	7.5	13.3	.610	20.1
5.	15.8	32.9	11.0	2.3	5.7	13.6	.610	23.0
.9	17.1	31.7	10.0	3.8	4. 3	13.7	.591	21.7
7.	19.5	29.2	9.77	6.4	3.0	13.1	.581	20.8
8.	24.4	24.4	10.7	13.3	2.2	11.1	.531	19.8
9.	29.2	19.5	9.77	20.1	1.4	9.05	.510	21.9
10.	34.1	14.6	10.0	27.6	2.6	6.52	. 508	3.5*
11.	39.0	9.7	11.0	34.6	0.9	4.40	.310	19.0
12.	43.9	4.9	11.0	41.6	0.2	2.34	.195	171.0*

¹MH = Morin ²Z = Moles o ³Y = Moles o

Z = Moles of uncombined Holmium (III) per liter

Y = Moles of uncombined Morin per liter

⁴Absorbance values and data were obtained from solutions used in the continuous variation study. * Not included in the calculation of the average value.

Table A-V. Estimated Equilibrium Ratio, K¹eq., Values of the Ytterbium (III) Morin Complex in 50-50

-

Estimated Equilibrium Ratio, K'_{eq.}, Values of the Ytterbium (III) Morin Complex in 50-50 DW at 25⁰ Table A-V.

Trial	Total Yb ⁺⁺⁺ Added M/l x 10 ⁶	Total MH ¹ Added M/1 x 10 ⁶	H ⁺ M/1 × 10 ⁶	Z ² M/1 × 10 ⁶	$rac{r}{M/1} \approx 10^{6}$	Yb(M) ⁺ M/1 × 10 ⁶	4 A419	K'eq.
l.	4.63	41.6	9.55	I I I I	30.4	5.62	. 235	8 9 9
2.	9.25	37.0	10.0		18.2	9.41	.351	1 1 1
3.	11.6	34.7	11.0	1.4	14.3	10.2	.400	4. 3*
4.	13.9	32.4	10.2	1.0	6.6	12.9	.457	30.9
5.	15.0	31.2	10.0	1.8	4.8	13.2	.466	31.8
6.	16.2	30.0	8.91	2.9	3.4	13.3	.467	31.5
7.	20.8	27.8	8.91	9.6	5.4	11.2	.398	31.8
8.	23.2	23.2	9.55	12.4	1.6	10.8	.378	31.7
9.	27.8	20.8	10.7	19.3	3.7	8.54	.302	3.7*
10.	32.4	13.9	10.0	25.9	0.9	6.42	. 228	31.1
11.	37.0	9.25	10.0	32.5	0.3	4.47	.156	14.3 [*]
12.	41.6	4.63	9.55	39.0	8 8 8	2.55	.083	1 1 1

¹MH = Morin

²Z = Moles of uncombined Ytterbium (III) per liter

³Y = Moles of uncombined Morin per liter

⁴Absorbance values and data were obtained from solutions used in the continuous variation study. Not included in the calculation of the average value.

~
² 2
at
A
'n
.50
50-
'n
X
ple
ы
Ŭ
rin
<u>_</u>
ž
H
ji
lη
ЧO
Ľ
fo
ta
Da
0
ati
Å
e e
<u> </u>
Ś
×
-
A
le
аb
H

	Excess Ho ((Morin)	(III), 4.850	<u>× 10-3 M</u> .		Excess Morir (Ho ⁺⁺⁺⁾	1, 1.32 × 10	-* M.
[rial	$M/1 \times 10^6$	Hq	A408	Trial	$M/1 \times 10^{6}$	μd	A408
1.	6.64	4.98	. 105	1.	0.00	5.05	.246
2.	14.3	5.05	.205	2.	1.26	5.97	. 292
3.	19.9	5.02	.309	3.	2.51	5.00	.325
4.	26.6	5.04	.412	4.	3.77	5.05	.383
5.	33.1	5.01	.518	5.	5.02	5.02	.424
6.	39.8	5.00	.620	6.	6.28	5.02	.460
7.	46.5	4.95	.719	7.	7.54	5.02	.502
8.	53.0	5.03	.825	8.	8.79	5.01	.550
9.	59.7	4.98	.926	.6	10.05	5.01	. 585
10.	66.4	4.97	1.02	10.	11.31	4.99	. 635
11.	72.9	4.98	1.13	11.	12.56	4.95	.675
12.	79.6	4.98	l.24	12.	13.82	4.99	.715

From Figure 29, slope of line 1, 1.55 x 10^4 , slope of line 2, 3.47 x 10^4 .

The ratio of the slopes is 1.00/2.24.

0 ū A- VI Table

~
25
at
DW
- 50
50.
in
omplex
ŭ
rin
f Q
2
Erbium
for
Data
Ratio
e
Slop
A-VII.
Table

	<u>Excess E</u> (Morin)	Jr(III), 4.780 x	10-3 M.			Ertt)	1.32 x 10-4	M.
Trial	M/1 × 10 ^t	hq è	A414	Tri	al N	√/1× 10 ⁶	μd	A414
1.	6.64	5.04	.125	l	•	0.00	5.01	.347
2.	14.3	4.98	. 262	5	•	1.20	5.01	.390
3.	19.9	5.02	.353	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	•	2.39	4.99	.436
4.	26.6	4.99	.483	4	•	3.59	4.96	.478
5.	33.1	4.95	. 600	шŋ	•	4.78	5.00	.516
6.	39.8	4.99	.713		•	5.98	5.02	.570
7.	46.5	5.00	.841		•	7.18	4.97	.609
8.	53.0	4.97	. 965		•	8.37	5.01	.652
9.	59.7	5.00	1.08	5.		9.57	4.98	.700
10.	66.4	4.99	1.20	10		10.76	4.96	.738
11.	72.9	4.98	1.33	11		.1.96	5.00	. 789
12.	79.6	4.98	1.43	12	-	13.16	5.00	.827
From	Figure 27,	slope of line 1,	1.82 x 10 ⁴ , slop	the of line 2, 3	63 x	10 ⁴ .		

The ratio of the slopes is 1.00 / 1.99.

	Excess Eu	(III), 5.263	x 10- ³ M.		Excess Morin	1, 1.32 × 10	-4 M.
Trial	(Morin) M/1 × 10 ⁶	Hd	A408	Trial	(Eu ⁺⁺⁺) M/1 × 10 ⁶	Hq	A408
l.	6.64	5.52	.123		0.00	5.45	.575
2.	9.54	5.55	.181	2.	1.24	5.53	.632
3.	14.3	5.47	.251	3.	2.47	5.48	.670
4.	16.6	5.55	.317	4.	3.71	5.50	.718
5.	19.9	5.53	. 365	5.	4.94	5.52	.775
6.	26.6	5.55	. 505	6.	6.18	5.50	.811
7.	33.1	5.54	. 608	7.	7.42	5.48	. 860
8.	39.8	5.52	.770	8.	8.65	5.52	.915
9.	46.5	5.45	. 890	9.	9.89	5.50	.955
10.	53.0	5.51	1.02	10.	11.12	5.46	1.01
11.	59.7	5.49	1.12	11.	12.36	5.49	1.05
12.	66.4	5.51	1.22	12.	13.60	5.48	1.10

Table A-VIII. Slope Ratio Data for Europium-Morin Complex in 50-50 DW at 25⁰

From Figure 28, slope of line 1, 1.89 x 10^{-4} , slope of line 2, 3.88 x 10^{4} . The ratio of the slopes is 1.00/2.05.

