A SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDY OF MORIN COMPLEXES OF TRIPOSITIVE CERIUM, NEODYMIUM, PRASEODYMIUM, SAMARIUM, TERBIUM AND THULIUM

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THESIS

ABSTRACT

A SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDY OF MORIN COMPLEXES OF TRIPOSITIVE CERIUM, NEODYMIUM, PRASEODYMIUM, SAMARIUM, TERBIUM AND THULIUM

by Margaret E. Tierney

Morin forms complexes with cerium (III), neodymium (III), praseodymium (III), samarium (III), terbium (III) and thulium (III). The effect of pH on the absorbance of these complexes and the nature of these complexes in 50 percent dioxane-50 percent water solutions were investigated.

Morin forms 1:2 complexes (lanthanide (III):morin) with these rare earth ions at pH 5.0 as determined by Job's method of continuous variations and confirmed by Harvey and Manning's slope-ratio method. The values of the equilibrium ratios for these complexes are 0.83, 4.3, 2.7, 7.9, 0.73 and 2.3 for cerium, neodymium, praseodymium, samarium, terbium and thulium, respectively.

The complexes fluoresce only slightly more than morin when exposed to 365, 436 mμ. or there absorption maximum wavelength radiation, while the complexes of lanthanum, gadolinium and lutetium flouresce significantly under these conditions.

The absorption band peak of morin occurs at 356 mμ., while the complex absorption band peaks for cerium and praseodymium, neodymium, samarium, terbium, and thulium occur at 413, 414, 415, 417, and 423 mμ., respectively.

A single isoabsorptive point exists in the absorption spectra of each of the complexes. The isoabsorptive point occurs at approximately 377 mμ.

The absorbances for the complexes change linearly with change in lanthanide (III) concentration over the approximate concentration range, 0 to 2.3×10^{-5} M., in the presence of excess morin, 1.32×10^{-4} M.

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By

Margaret E. Tierney

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VITA

Name: Margaret E. Tierney

Born: Sept. 21, 1943 in New Britain, Connecticut

Academic Career: Regina High School, Hyattsville, Maryland (1957-1961)

Chestnut Hill College, Philadelphia, Pennsylvania (1961-1965)

Michigan State University, East Lansing, Michigan (1965-)

Degree Held: B. S. Chestnut Hill College (1965)

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INTRODUCTION

The rare earths or lanthanides have been very difficult to separate because of their great similarities in chemical properties under usual conditions. These great similarities are due to the shielded nature of the 4f subshell which is filled with electrons as the lanthanide series progresses from lanthanum to lutetium.

Before 1945 these elements were frequently determined as a group with a nonselective precipitant. The oxalate method was the most extensively studied. The lanthanides were precipitated as their oxalates with oxalic acid (1), ammonium oxalate (2), dimethyl oxalate (3), or diethyl oxalate (4). Occasionally they were precipitated as fluorides or hydrous oxides.

Nonselective titrimetric methods have been used to determine the rare earth elements as a group. Ethylenediaminetetraacetic acid (EDTA) is the most frequently used titrant. Many indicators have been developed for this method (5-15). Complexone III (16-18) and Trilon B (19-22) are also common titrating agents.

Better methods than the classical methods of fractional crystallization and fractional precipitation have been developed for separating the rare earths. Some separations are effected by oxidation or reduction to anomalous oxidation states (states other than tripositive). Another method is liquid-liquid extraction, often with tributyl phosphate.

Extraction separations have been enhanced using reagents that form complexes with the rare earths. The most modern method is ion exchange chromatography. Ion exchange separations have also been sharpened using complexing agents such as morin (23), EDTA, (24-26) and 8-hydroxyquinoline (27). Several books summarize the advances in separation of the lanthanides (28-30). With more abundant quantities of high purity rare earths available, it is possible to study more effectively the individual elements and determine trends in the properties of the lanthanide series.

The fluorescence spectra of rare earth compounds have been known since the 1930's. However, analytical applications have been few since the fluorescence spectra are weak. In qualitative detection tests, only lanthanum (III), gadolinium (III) and lutetium (III) formed fluorescent complexes with morin (2',4';3,5,7-pentahydroxyflavone) (31). The other lanthanide (III)-morin complexes did not fluoresce due to internal quenching caused by intramolecular energy transfer.

There are two methods of spectrophotometric analysis for the rare earth elements. One method utilizes the band absorption spectra of the colored ions. The spectra of aqueous solutions are complex, extending from the ultraviolet to the infrared region. The spectra of the lanthanide (III) perchlorates (32-38), chlorides (33,34,38-43), nitrates (33,44,45) and acetates (33) are well known.

The molar absorptivities of the lanthanide (III) ions are low, ranging from approximately one to ten (29). Thus the absorption bands are not applicable for the determination of micro quantities of lanthanides.

The second spectrophotometric method for lanthanide analysis utilizes the formation of intensely absorbing complexes. The formation of lanthanide (III) complexes in solution leads to modifications in the ligand absorption spectra, since the complexes generally absorb light at different wavelengths than the chelating ligands.

A variety of chromophoric agents are available for determination of the rare earths. These elements have been determined using Xylenol Orange (46-54), Alizarin Red S (55-58), 3-nitroalizarin (59), salicylic acid derivatives (60-63), Aluminon (57,63-65), naphthazarin (66), oxidized Haematoxylin (67), Chrome Azurol S (57,68-70), Pyrocatechol Blue (71), Methylthymol Blue (72-73), Thymolphthalexon (74), Erichrome Black T (75), Naphthyl azoxine S (76), Chromotrope B (57,77), Pontacyl Violet (78), Arsenazo (79-82), PAR (83), Stilbazo (84), dinitropyrylazo (85), 5,7-dibromohydroxyquinoline (86) and Thoron (57). These elements have also been determined using EDTA and several related acetic acid derivatives (87-98). Morin has been used for spectrophotometric and spectrofluorometric determination of the rare earths and other elements (99-103).

The purpose of this investigation is to extend the studies of the complexation reactions between morin and lanthanide (III) ions in 50-50 dioxane-water begun by Fleck (99), Weiler (100) and Van Eenenaam (101). A study was undertaken to establish light absorption and fluorescence characteristics of the complexes formed between morin and cerium, neodymium, praseodymium, samarium, terbium and thulium.

HISTORICAL

Several books have been published concerning fluorescence phenomena. Pringsheim discussed the theoretical aspects of fluorescence, including a chapter on the lanthanide elements (104). Fluorescence is also discussed by Bowen and Wokes (105). Hercules has edited a book on the topic (106). In addition, C. E. White reviews both organic and inorganic applications of fluorometric analysis in "Analytical Chemistry" (107,108). Poluektov and Kononenko also reviewed the fluorescence of rare earth chelates (109). Multitudinous references are cited in these review articles.

The lanthanides form many complexes with β-diketones (110-119). Prominent among these complexes are those with thenoyltrifluoroacetone, benzoyltrifluoroacetone and dibenzoylmethane. Major investigations of these complexes have been performed by Crosby and Whan (120,121) and Kononenko and Poluektov (122-124). Crosby and Whan propose the theory that the triplet state of the complex must be above the resonance level of the lanthanide for fluorescence to occur. Many of these complexes do fluoresce and this property has made them important in the development of lasers (125-129).

Fluorescence is observed for morin complexes with lanthanum (III), gadolinium (III) and lutetium (III) (31,99-101,130). For the other lanthanide-morin complexes there is considerably less, if any, fluorescence.

Katyal has reviewed the use of flavones as analytical reagents (103). The complex of morin with gallium has been

studied by Akhmedli and Bashirov (131) and by Akhmedli and Glushchenko (132). Dombi and Kozema have studied the reaction of morin with aluminum (133,134). Mary Fletcher conducted a fluorometric investigation of the beryllium-morin system (135). Nowicka-Jankowska (136) and his coworkers have reported 1:1 complexes of morin with praseodymium (III), gadolinium (III), yttrium (III) and holmium (III).

Milkey and Fletcher (102) conducted an investigation of the thorium (IV)-morin complex in slightly acidic ethanol-water mixtures. Their investigation and the work of Fleck (99), Weiler (100) and Van Eenanaam (101) was used as a pattern for this study.

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 (137). Vosburg and Cooper (138) and Katzin and Gebert (139) have extended Job's method to systems in which more than one complex is formed.

Bent and French (140) determined the composition and dissociation constant of ferric thiocyanate by varying the concentration of thiocyanate with a constant concentration of iron and then 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 logarithm of the total thiocyanate concentration was plotted against the lograithm of the absorbance, constants having been added to both axes to give a line intersecting the origin.

The mole-ratio method applicable to very slightly dissociated complexes is attributed to Yoe and Jones (141). The absorbance is plotted as a function of the ratio of total concentration of anion to cation. A break in the curve is obtained at the stoichiometric ratio of anion to cation.

Equimolar solutions have been employed by several scientists to determine stability constants. Hagenmuller (142,143) developed a method using equimolar solutions that is restricted to 1:1 complexes. A series of mixtures of the two substances capable of forming complexes is prepared and an additive physical property determined. The position of the maximum of the curve representing the differences between the observed values and those which correspond to the rule of mixtures indicates the mole ratio of the two original substances in the compound. The method of Betts and Michels (144) is similar to Hagenmuller's, but does not employ equimolar solutions. Shaeppi and Treadwell (145) also developed a method using equimolar solutions. Schwarzenbach (146) developed the restrictions for their method (145) when a 1:1 complex is formed.

Another method of establishing the composition of complexes is the slope-ratio method of Harvey and Manning (147). The absorbance of the complex is plotted against varying concentrations of ligand holding metal ion concentration constant, and against varying concentrations of metal ion holding ligand concentration constant. The slope of the line obtained in the presence of excess metal ion represents the change in absorbance per mole of ligand. The slope of the line obtained in the presence of excess ligand represents the change in absorbance per mole of metal ion. The ratio of the slope of the line representing the change per mole of morin to the slope of the line representing the change per mole of metal ion indicates the ratio of metal ion to ligand in the complex.

EXPERIMENTAL

Instrumentation

The spectrofluorometer used for this research is a double monochromator instrument designed and constructed by Mr. J. Holland of Michigan State University. Figure 1 shows a block diagram of the instrument which illustrates the excitation and fluorescent emission light paths. The spectrofluorometer consists of the following components:

1. An Osram XBO-150 xenon arc lamp ultraviolet source powered by a Sola model 67-10-109 power supply with the lamp mounted in a standard Bausch and Lomb housing and cooled by an air circulating fan;
2. Bausch and Lomb model 33-86-45-58 grating monochromators with both gratings blazed at 3000 Å.;
3. A custom made brass cell holder, with provision for constant temperature regulation, to hold Pyrocell clear-window 10 mm. silica cells made especially for fluorometry;
4. An RCA 1P28 photomultiplier tube mounted in a light-tight housing attached to the emission monochromator as illustrated;
5. The detector electronics system consisting of a Philbrick P25A operational amplifier used in a follower mode and an Analogue Device #210 operational amplifier used as a unity gain filter amplifier;
6. A Sargent SR recorder.

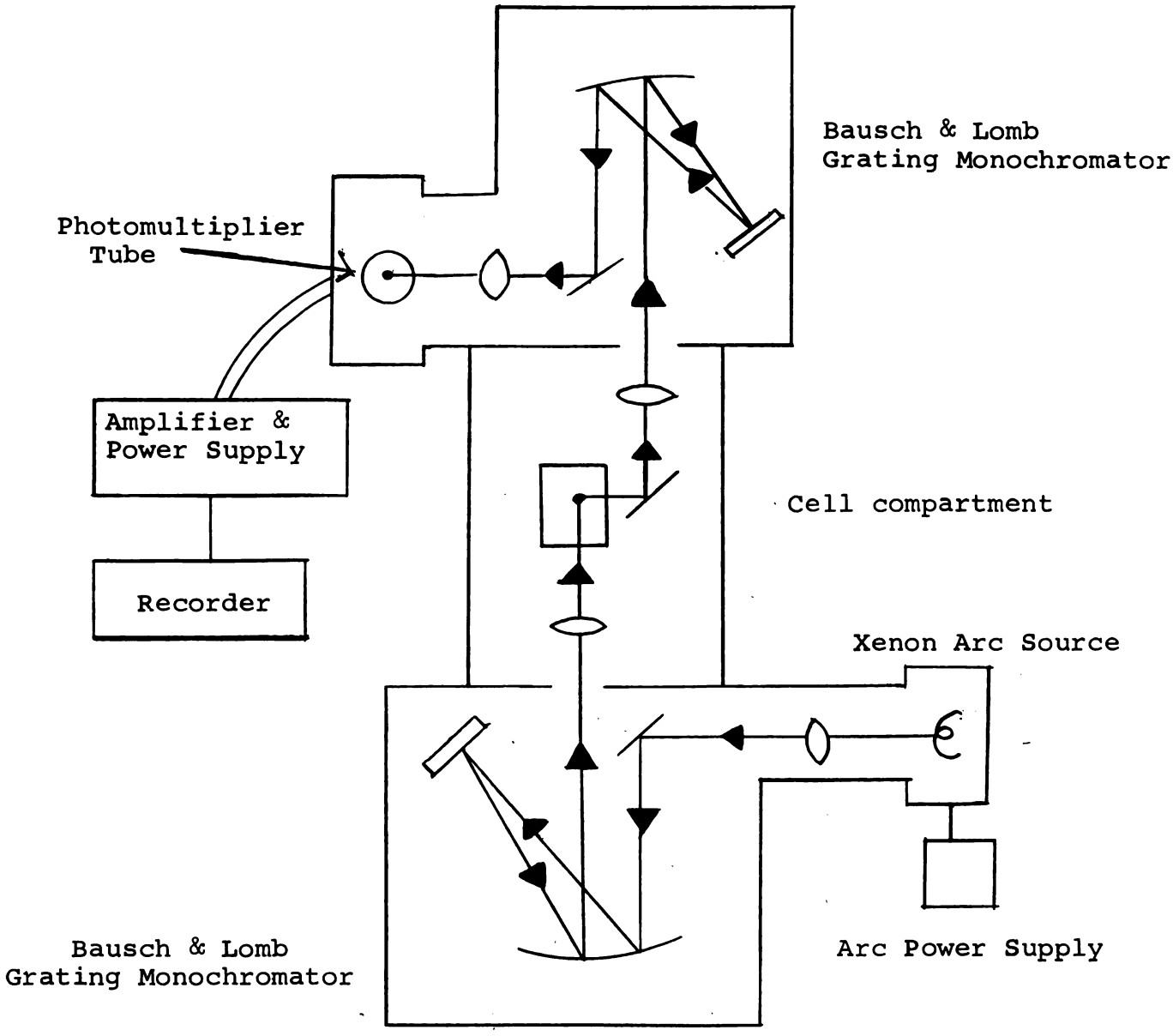

Figure 1. Block diagram of Spectrofluorometer.

Cary Model 14 recording spectrophotometer was used for all absorption measurements. A matched pair of Beckman standard blue silica cells having a pathlength of 1.000 ± 0.005 cm. 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 ± 0.02°C.

A Beckman Model 76 expanded scale pH meter equipped with a glass-saturated calomel microelectrode pair or with a micro-combination electrode was used for all pH measurements. The instrument was calibrated with Beckman or Fisher Certified pH 4 buffer.

Reagents

Ammonium Hydroxide

Baker's Analyzed Reagent Grade, assay 29.9% as NH_3, distilled and stored in a polyethylene bottle equipped with an ascarite protection bulb.

Cerous Perchlorate (Hydrated)

G. Frederick Smith's Reagent Grade.

2',7'-Dichlorofluorescein

Eastman Kodak White Label.

p-Dioxane

Fisher Certified Grade.

Eastman Kodak White Label.

Lanthanum Oxide

Optical Grade, Heavy Minerals Company, Chattanooga, Tennessee.

Morin Dihydrate

Dr. Theodor Schuchardt, Munich, Germany.

Neodymium, Praseodymium, Samarium, Terbium and Thulium Oxides

Michigan Chemical Corporation , St. Louis, Michigan.

Perchloric Acid

Baker and Adamson's Reagent Grade, 70-72%.

Mallinckrodt's Reagent Grade, 70-72%.

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 (148) developed by Fieser (149) was used to purify certified 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, potassium hydroxide pellets were 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 an amber screw-cap bottle containing a layer of 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 ± 0.5°C. It was stored in amber glass-stoppered bottles.

Lanthanide Oxides

Portions of the various oxides were weighed and dissolved in a minimum amount of perchloric acid. For Ce(III) a portion of the perchlorate was weighed and dissolved in a minimum amount of perchloric acid. The above solutions were diluted and aliquots titrated with a 0.0503 M solution of primary standard disodium ethylenediaminetetraacetate (150) to the xylenol orange endpoint (87). Aliquots of these standardized solutions were taken for the preparation of the working solutions of 10.0, 1.0, 0.1 and 0.01 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 morin.

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 performed at $25 \pm 1^{\circ}C$. All solutions were equilibrated in a constant temperature bath maintained at $25 \pm 0.02^{\circ}C$ for a minimum of one-half hour before making measurements.

Method of Sample Preparation

The desired volume of morin solution was transferred into a 25 ml. volumetric flask. Pure dioxane was added to give a total dioxane volume of 12.5 ml. The desired volume of lanthanide perchlorate solution was added and then distilled water until the total volume was 21-22 ml. The solution was transferred to a 30 ml. beaker where the pH was adjusted to 5.0 with dilute ammonium hydroxide and/or perchloric acid. The resulting solution was transferred back to the 25 ml. flask and the sample diluted to the mark. The pH of the sample was checked after equilibration in the thermostated water bath.

Instrumental Measurements

Spectrophotometric Measurements. The instrument was allowed to warm up for at least 20 minutes to insure instrumental stability. The baseline was set to zero with light passing through solvent solution of 50-50 dioxane and water at pH 5.0 in both reference and sample beams.

Spectrofluorometric Measurements. To standardize the instrument the excitation monochromator was set at 335 mμ (one of the strong peaks of dichlorofluorescein), while the emission monochromator was set at 520 mμ. The xenon lamp, power supply, amplifiers and detector were warmed up for at least 20 minutes to insure stability. The 0.5 γ per ml. dichlorofluorescein solution was placed in the cell, the shutter opened and the instrument adjusted to give a readout of 60. The value of 60 was chosen so that a solution of lanthanum-morin complex at pH 5.0 would yield a fluorescence spectrum (Figure 8) of the same magnitude as that obtained for the same concentration solution in previous studies employing a different spectrofluorometer. Instrumental readings were recorded as relative fluorescence intensities.

Nature of the Complex

Isoabsorptive Point. In order to determine the number of complexes formed and whether the reaction is stoichiometric, a series of solutions containing 400 γ of morin and

amounts of lanthanide (III) varying between 0 and 100 γ per 25 ml. were prepared and adjusted to pH 5.0.

Method of Continuous Variations. Job's method of continuous variations (137) was employed to determine the empirical formula of the complex formed. The absorbances for praseodynium (III) and cerium (III) systems were measured at 356, 390 and 413 mμ, for the neodymium (III) system at 356, 390 and 414 mμ, for the samarium (III) system at 356, 390 and 415 mμ, for the terbium (III) system at 356, 390 and 417 mμ, and the thulium (III) system at 356, 390 and 423 mμ. The total concentration of lanthanide (III) ion and morin was maintained constant at approximately 54×10^{-6} M, the actual value differing slightly for each lanthanide (III) ion.

Slope Ratio Method. To confirm the composition of the complexes, the slope-ratio method of Harvey and Manning (147) was employed. A series of solutions containing lanthanide (III) ranging in concentration from approximately 0.2×10^{-5} M to 2.3×10^{-5} M in the presence of a large excess of morin, 1.32×10^{-4} M , were prepared. The absorbances of these solutions, measured at the desired wavelength, were plotted against the concentration of lanthanide (III) ion, and the slope of the line determined. A series of solutions containing morin in the concentration range of approximately 0.6×10^{-5} M to 5.3×10^{-5} M in the presence of a large

excess of lanthanide (III) ion were also prepared. The absorbances were plotted against the concentration of morin and the slope of the line determined. The ratio of the slopes of the two lines was then determined to obtain the ratio of lanthanide (III) ion to morin in the complex.

DISCUSSION OF RESULTS

General

Morin (2',4',3,5,7-pentahydroxyflavone) forms complexes with cerium, neodymium, praseodymium, samarium, terbium and thulium. The absorption spectra of morin and the complexes are shown in Figures 2-4. The complexing agent has an absorption peak at 356 mμ. 413, 414, 415, 417, and 423 mμ. are the absorption peak wavelengths for the cerium and praseodymium, neodymium, samarium, terbium, and thulium complexes, respectively.

Figure 8 shows that the lanthanum-morin complex fluoresces significantly when exposed to ultraviolet radiation as Fleck (99) also observed. Weiler (100) observed fluorescence from the morin complexes of gadolinium and lutetium. Morin fluoresces to a slight extent under the experimental conditions as illustrated in Figure 15. Figures 9-14 show that the rare earth complexes under investigation do not fluoresce much more than morin. These results confirm the observations of Pollard *et al.* (31) who ran qualitative tests to determine whether lanthanide-morin complexes fluoresced when illuminated with ultraviolet radiation. Van Eenanaam (101) also demonstrated that the morin complexed dysprosium, erbium, europium, holmium and ytterbium fluoresced very weakly.

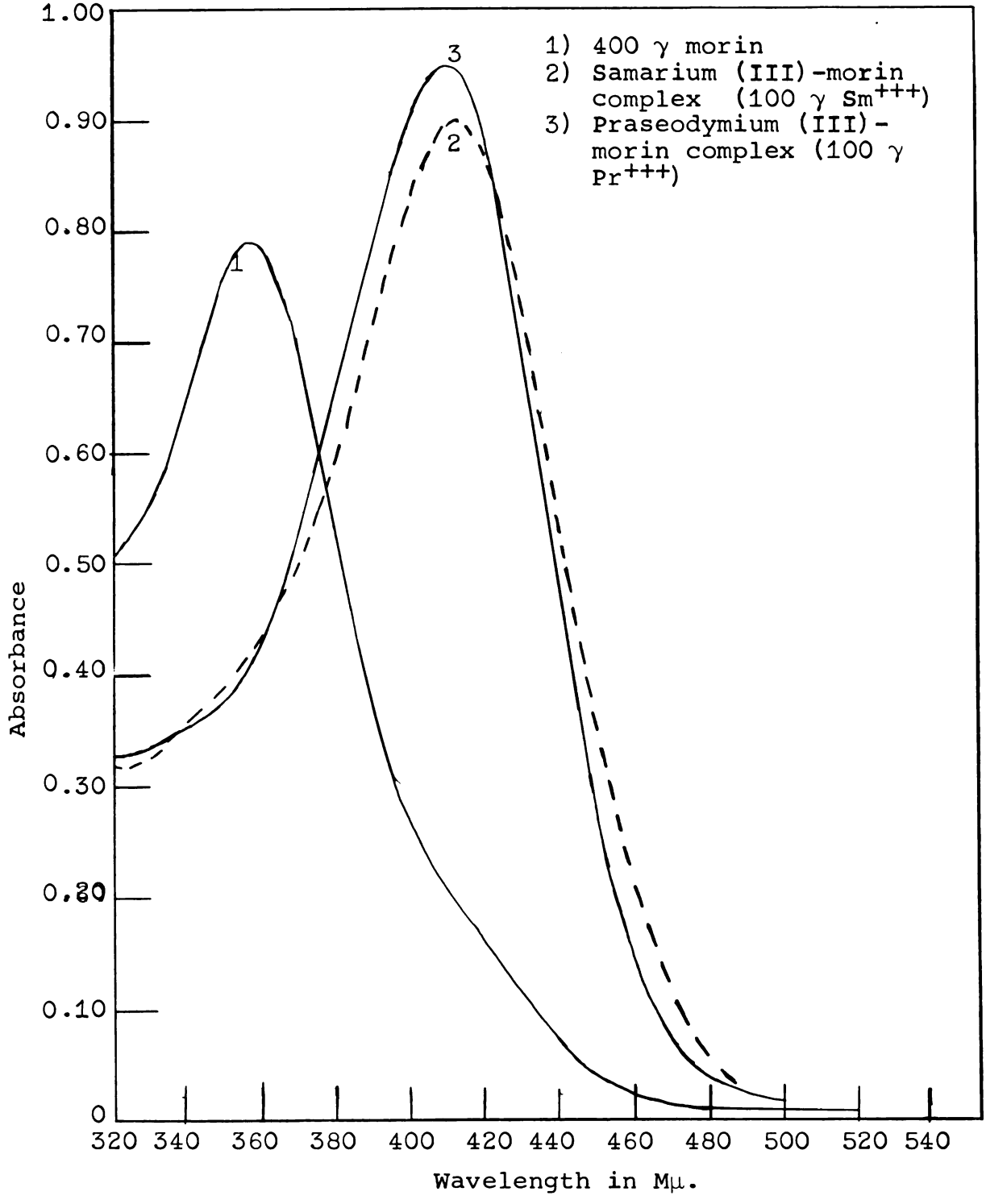

Figure 2. Absorption spectra of morin and the complexes of morin with samarium (III) and praseodymium (III) in 50-50 DW at pH 5.0.

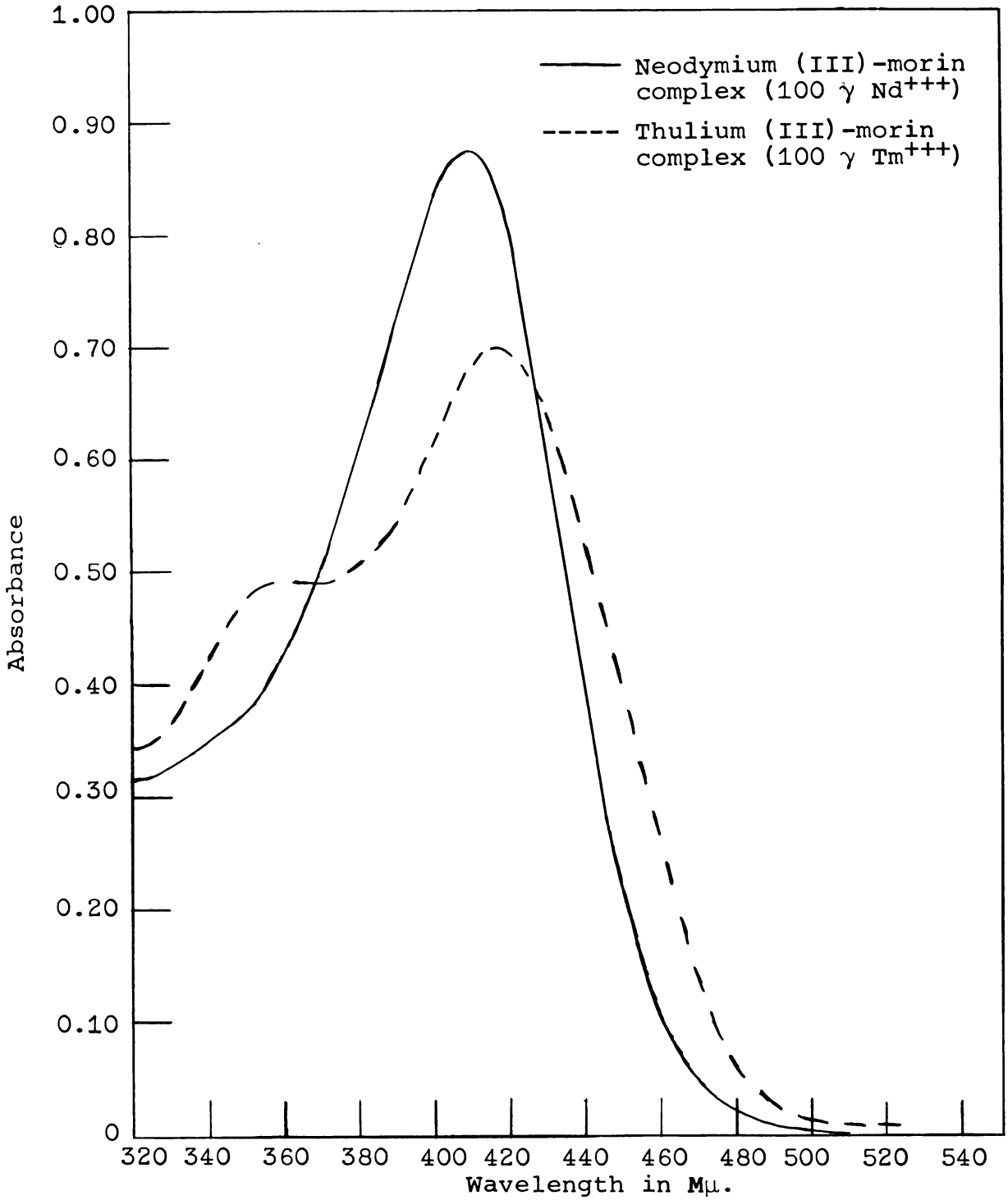

Figure 3. Absorption spectra of the complexes of morin with neodymium (III) and thulium (III) in 50-50 DW at pH 5.0.

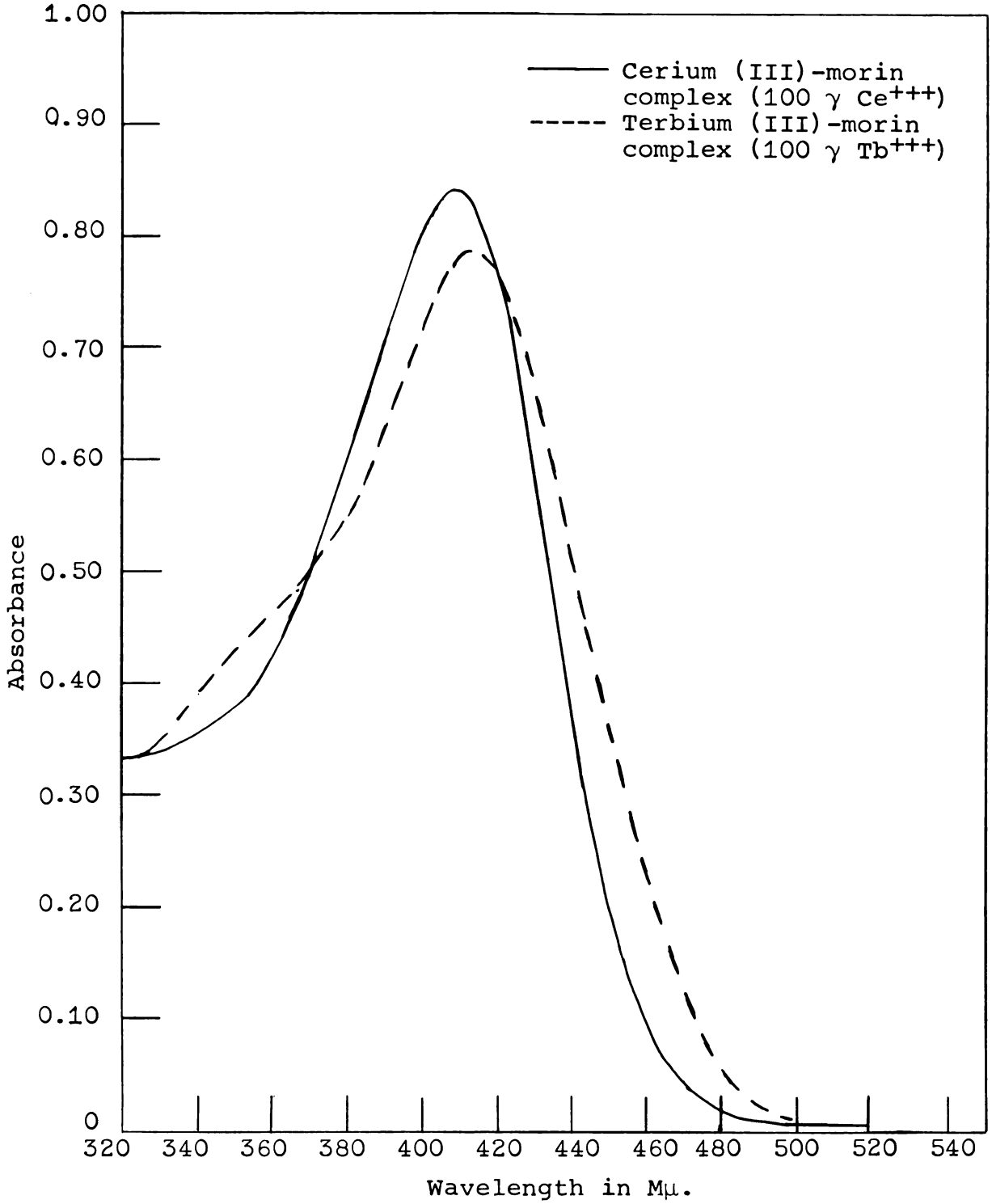

Figure 4. Absorption spectra of the complexes of morin with terbium (III) and cerium (III) in 50-50 DW at pH 5.0.

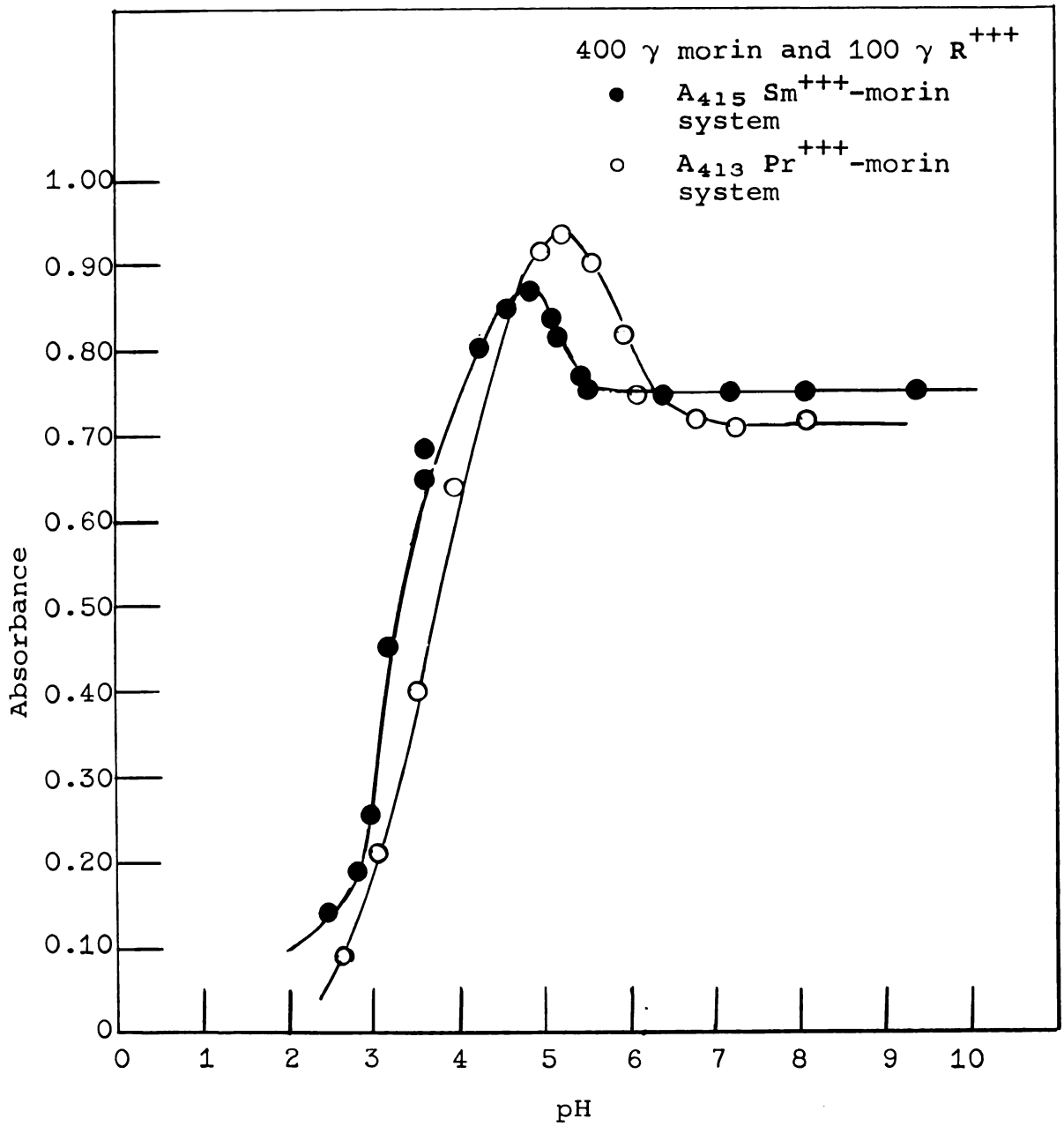

Figure 5. Effect of pH on the absorbance of the complexes of morin with samarium (III) and praseodymium (III) in 50-50 DW.

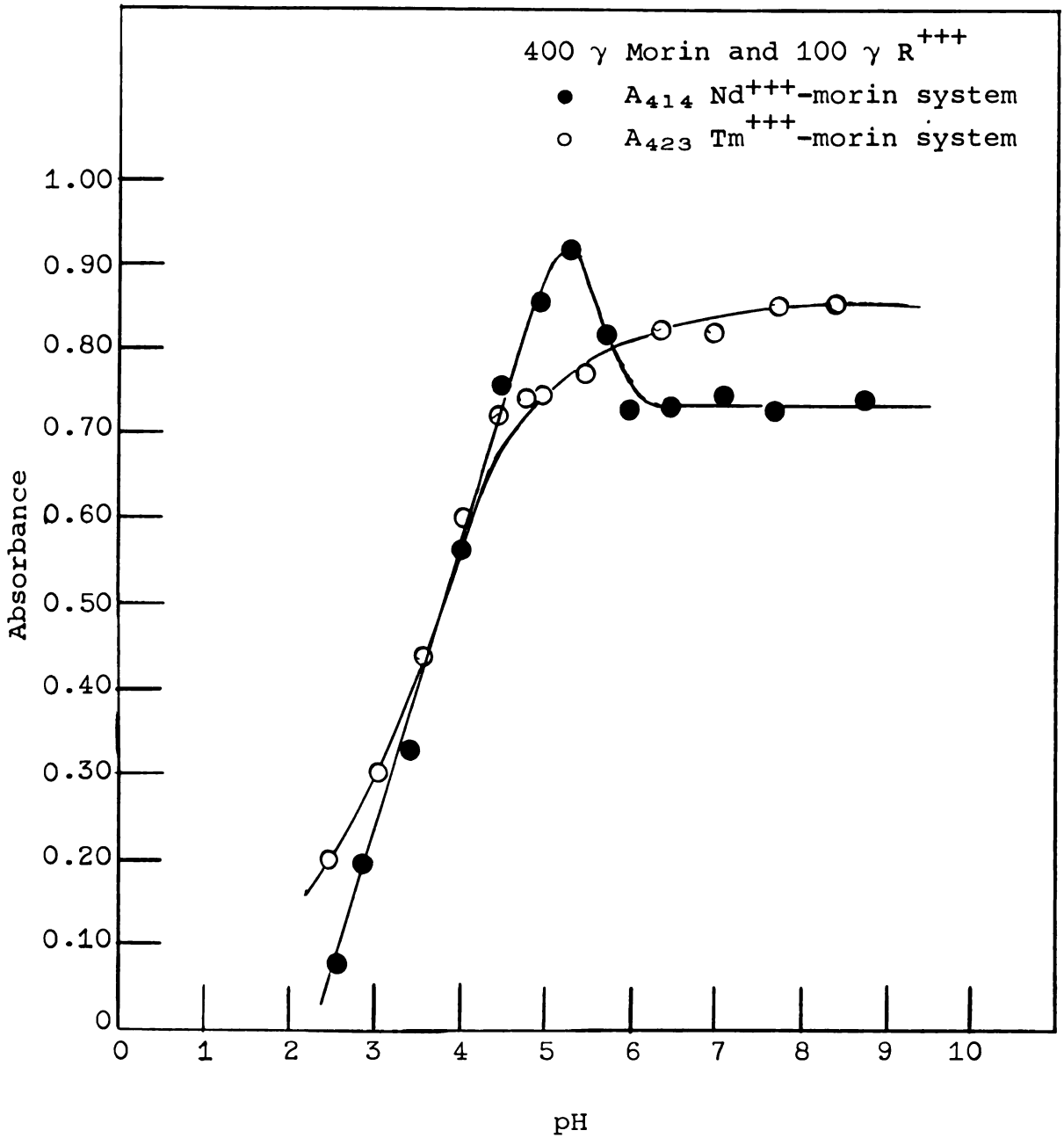

Figure 6. Effect of pH on the absorbance of the complexes of morin with neodymium (III) and thulium (III) in 50-50 DW.

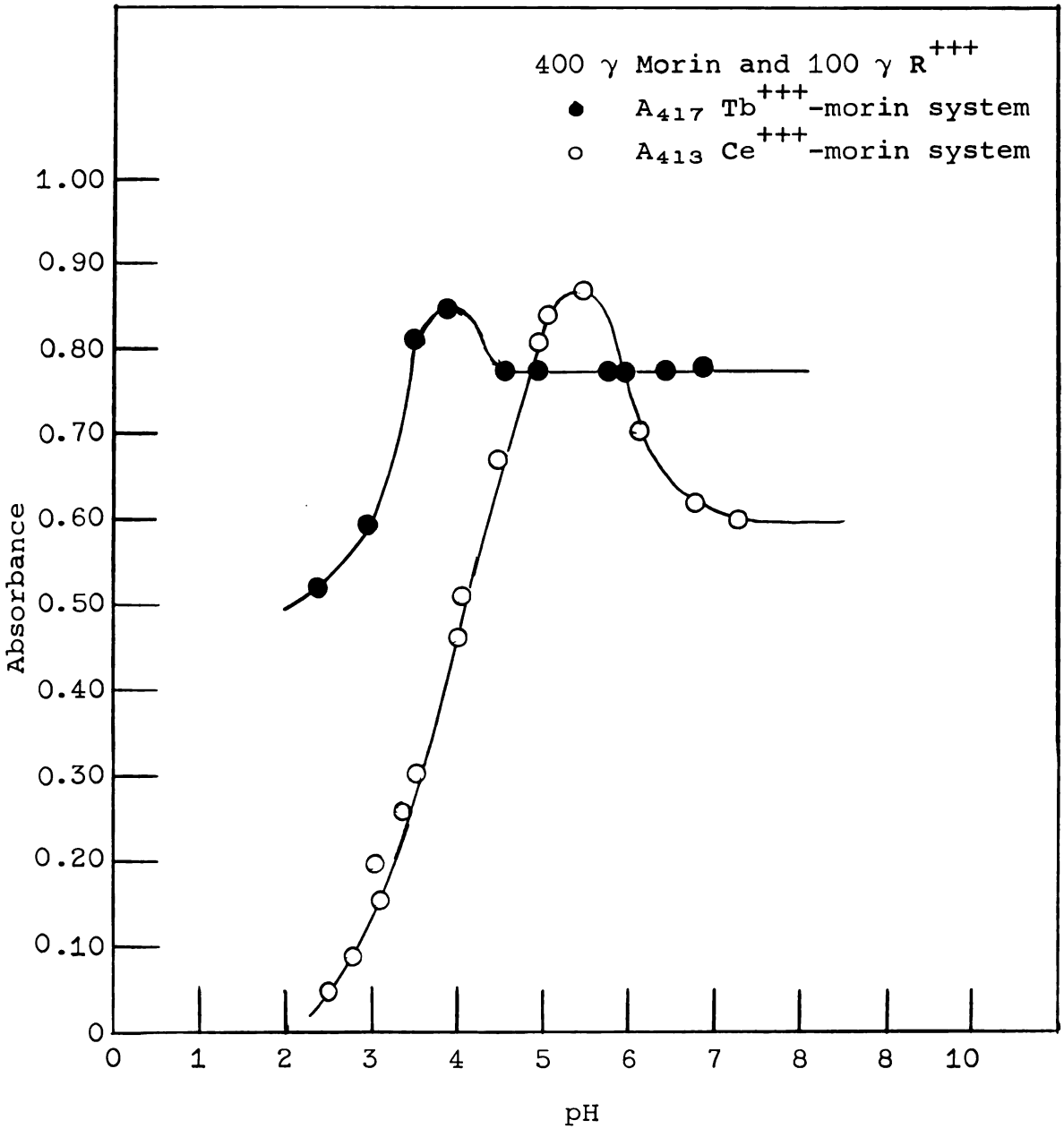

Figure 7. Effect of pH on the absorbance of the complexes of morin with terbium (III) and cerium (III) in 50-50 DW.

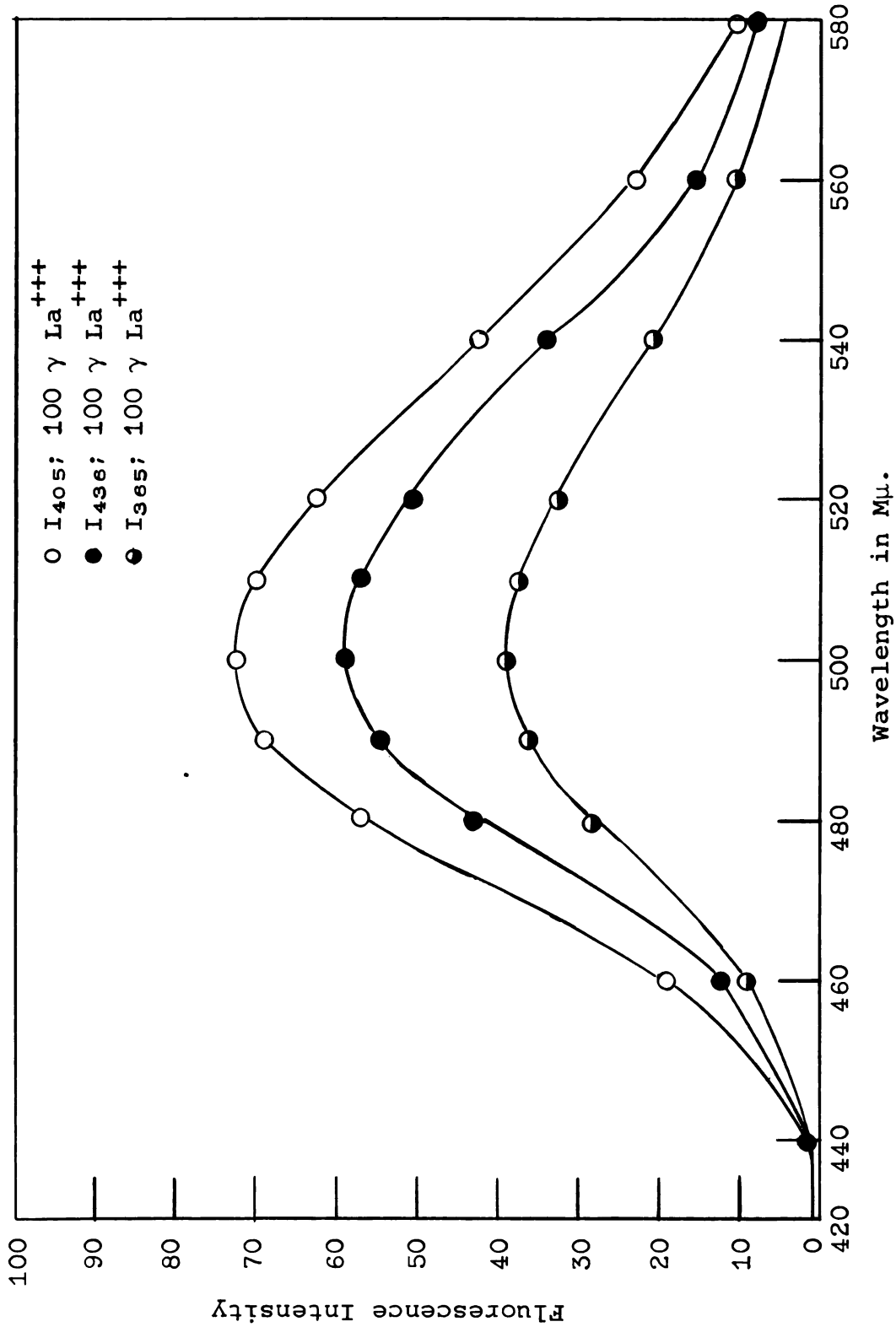

Figure 8. Fluorescence spectra of the complex of morin with lanthanum (III) in 50-50 DW at pH 5.0.

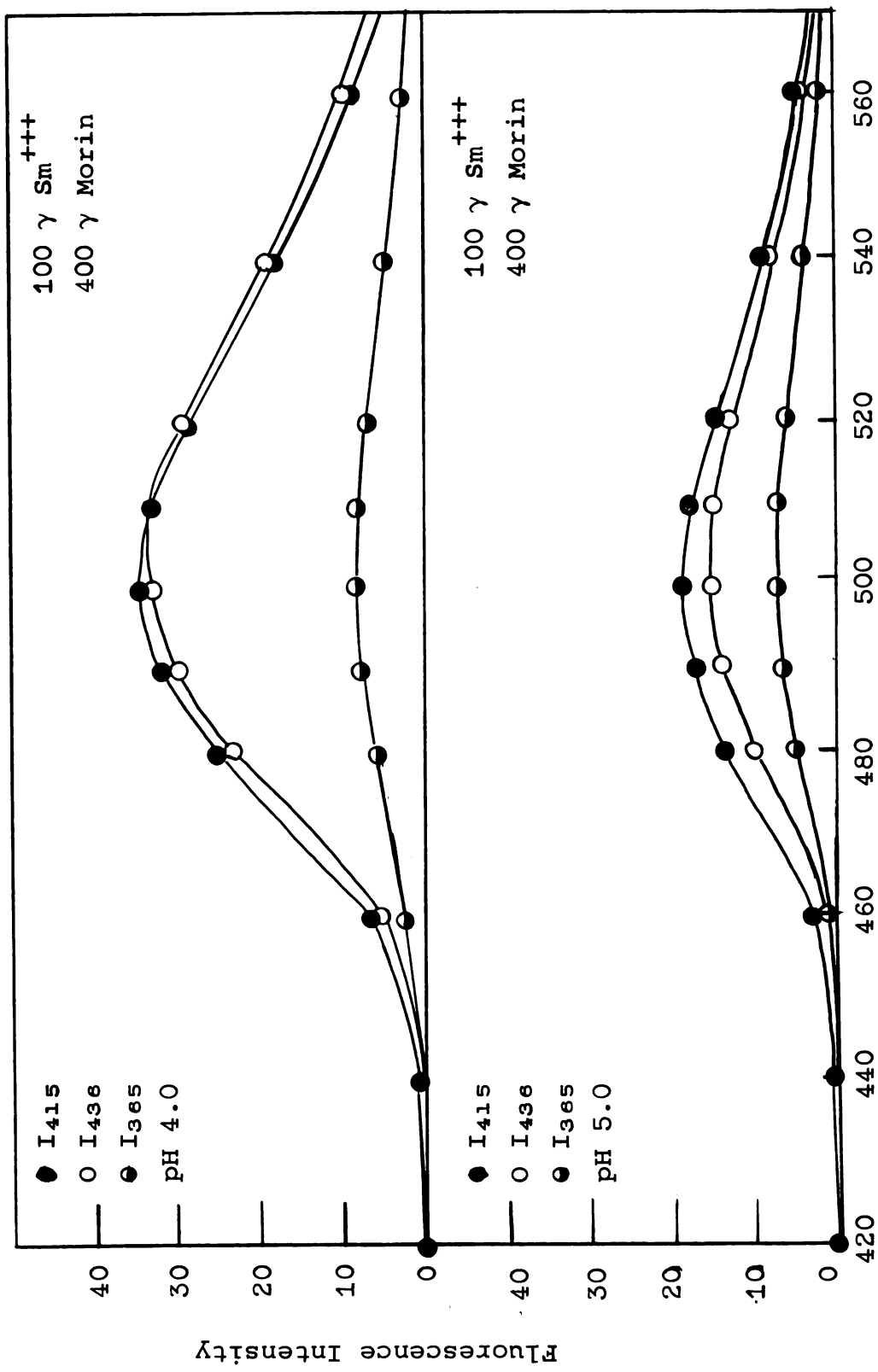

Figure 9. Fluorescence spectra of the complex of morin with samarium (III) in 50-50 DW.

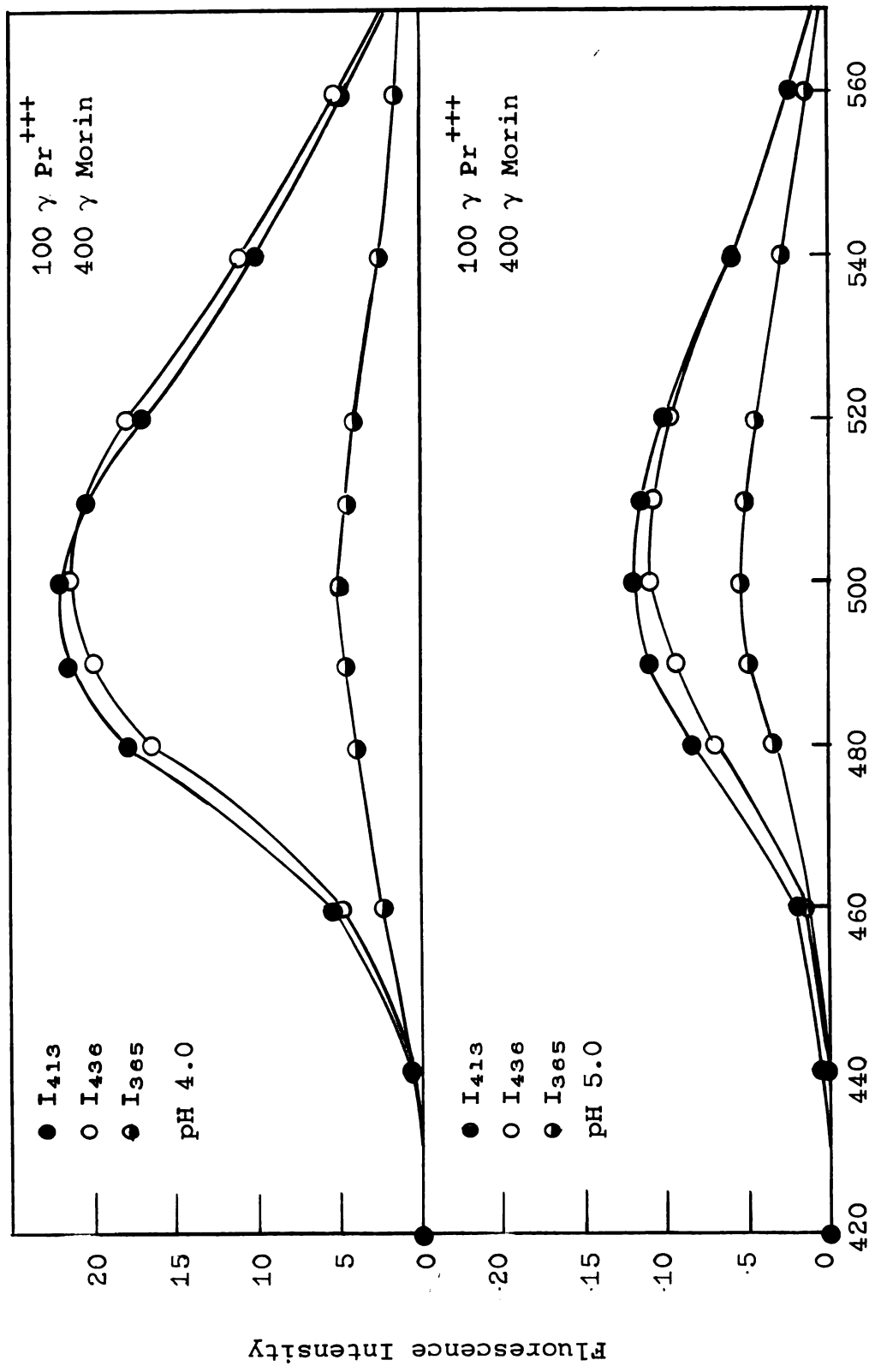

Figure 10. Fluorescence spectra of the complex of morin with praseodymium (III) in 50-50 DW.

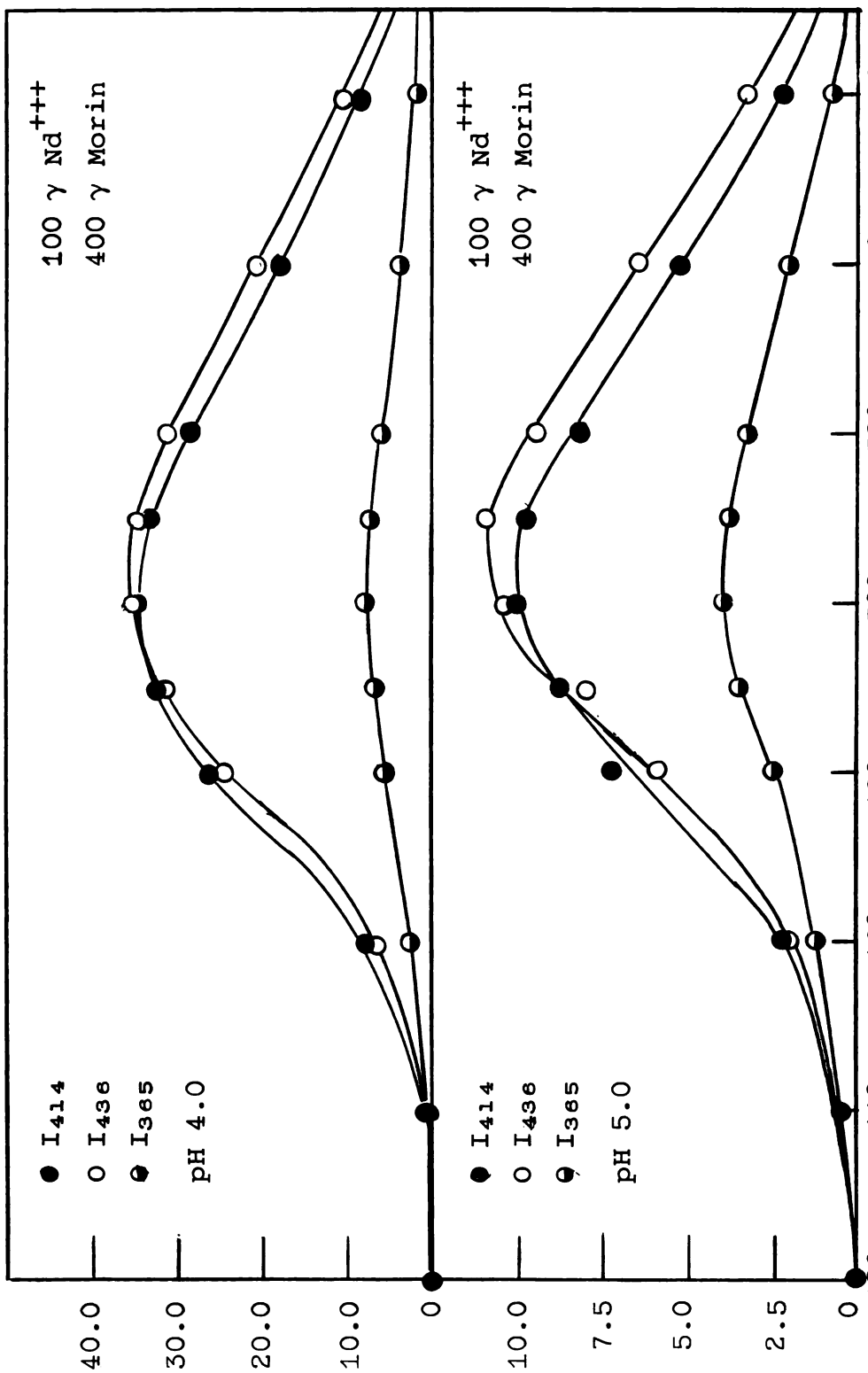

Figure 11. Fluorescence spectra of the complex of morin with neodymium (III) in 50-50 DW.

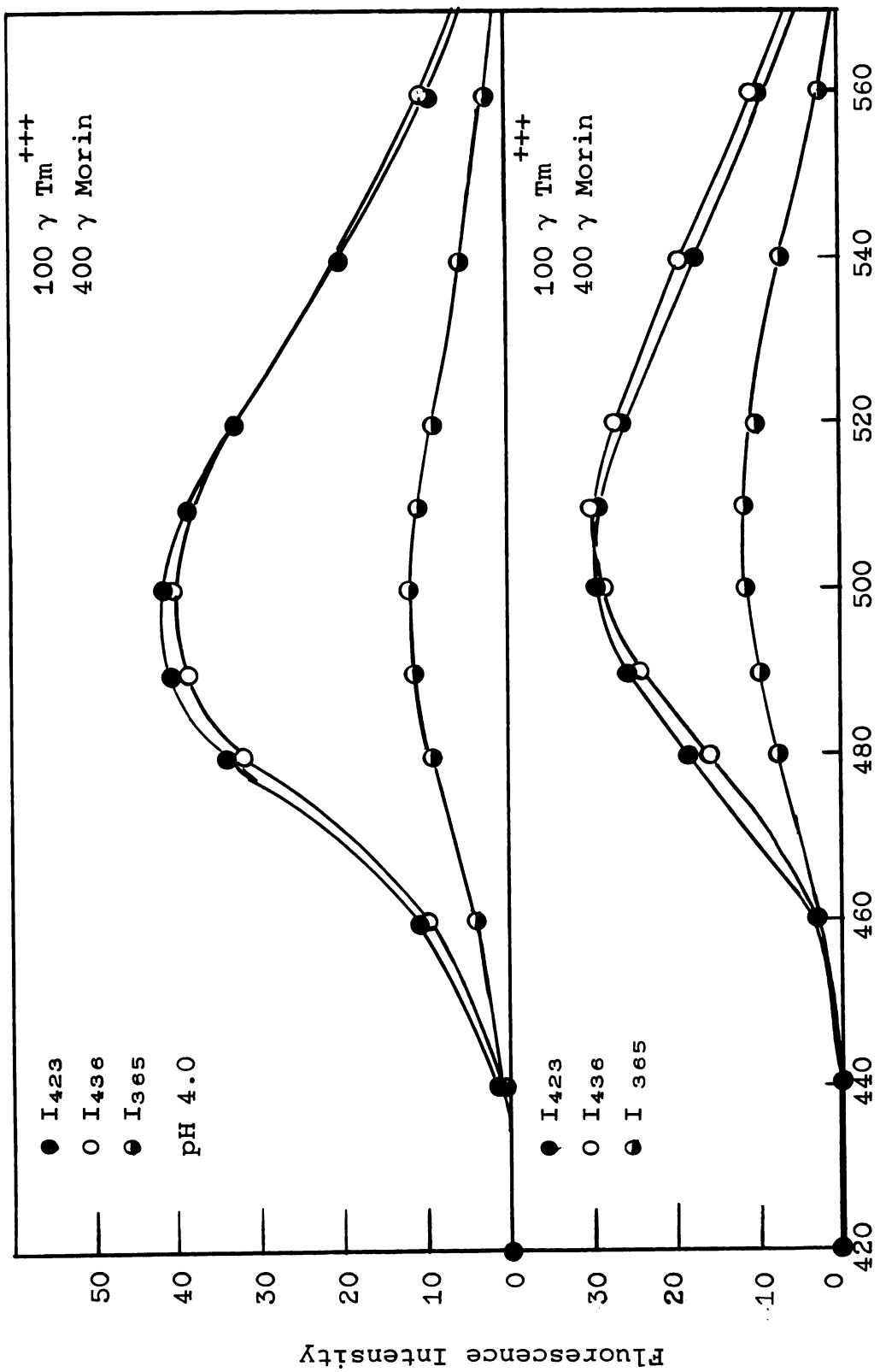

Figure 12. Fluorescence spectra of the complex of morin with Thulium (III) in 50-50 DW.

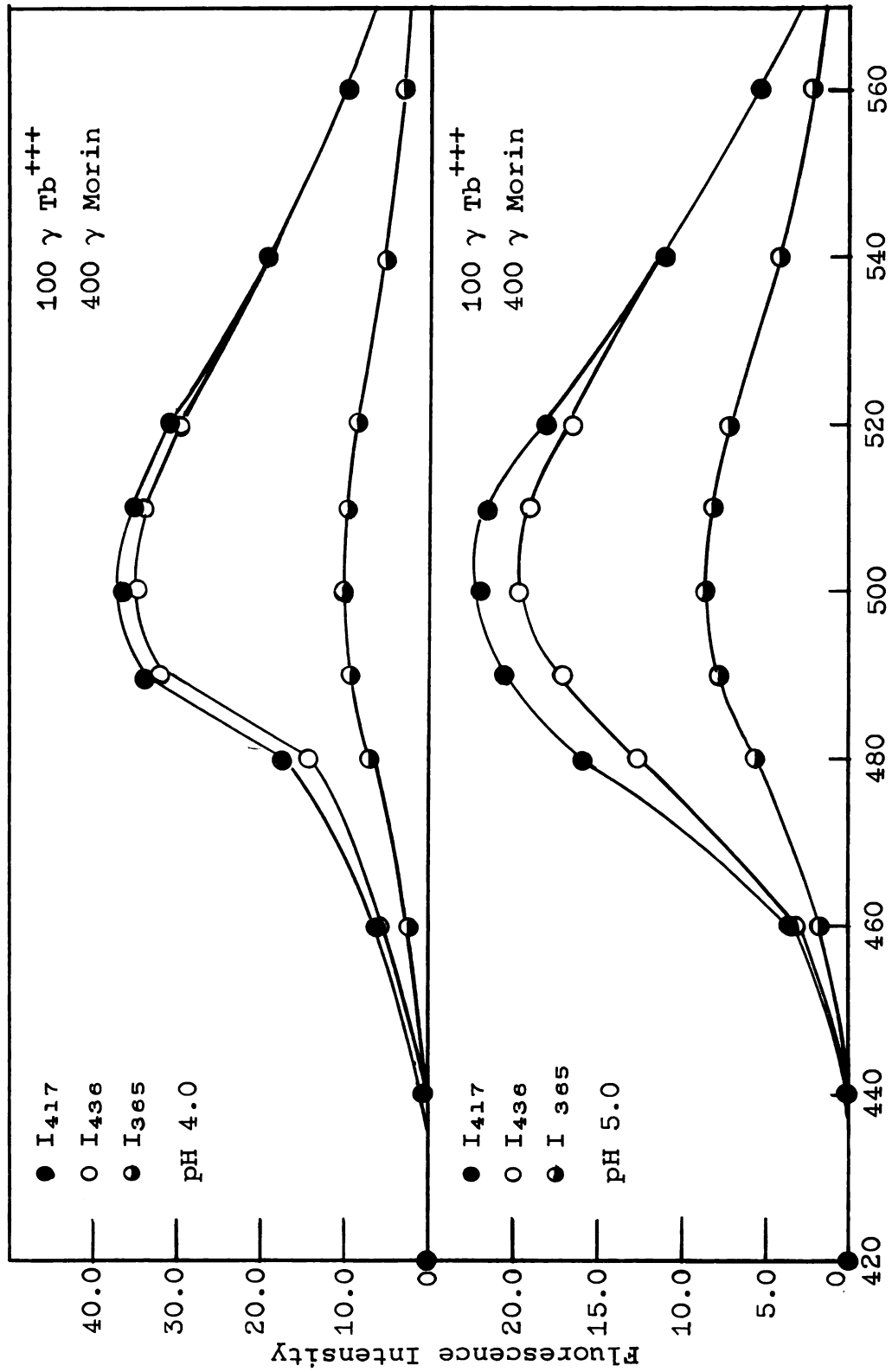

Figure 13. Fluorescence spectra of the complex of morin with terbium (III) in 50-50 DW.

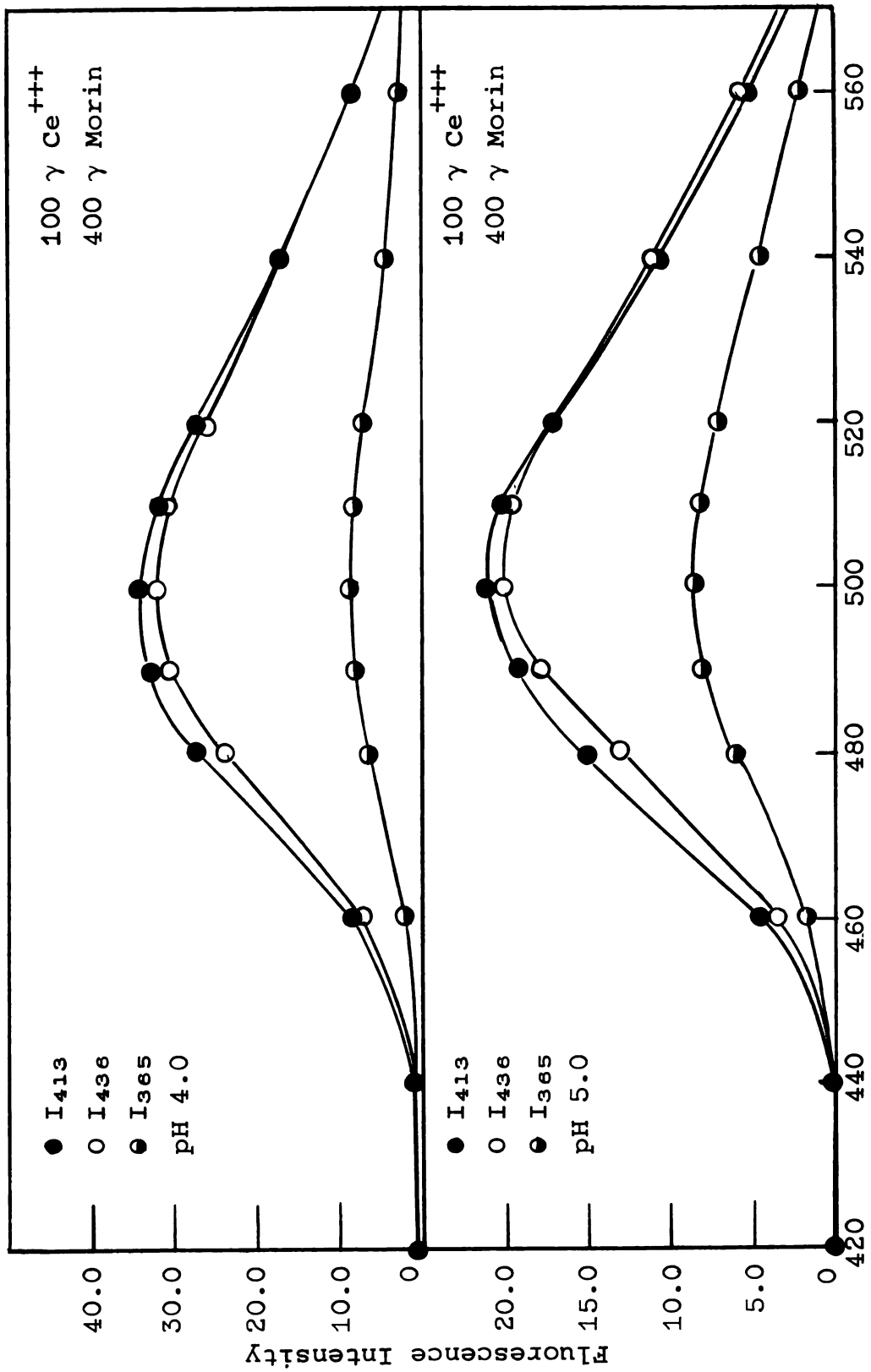

Figure 14. Fluorescence spectra of the complex of morin with cerium (III) in 50-50 DW.

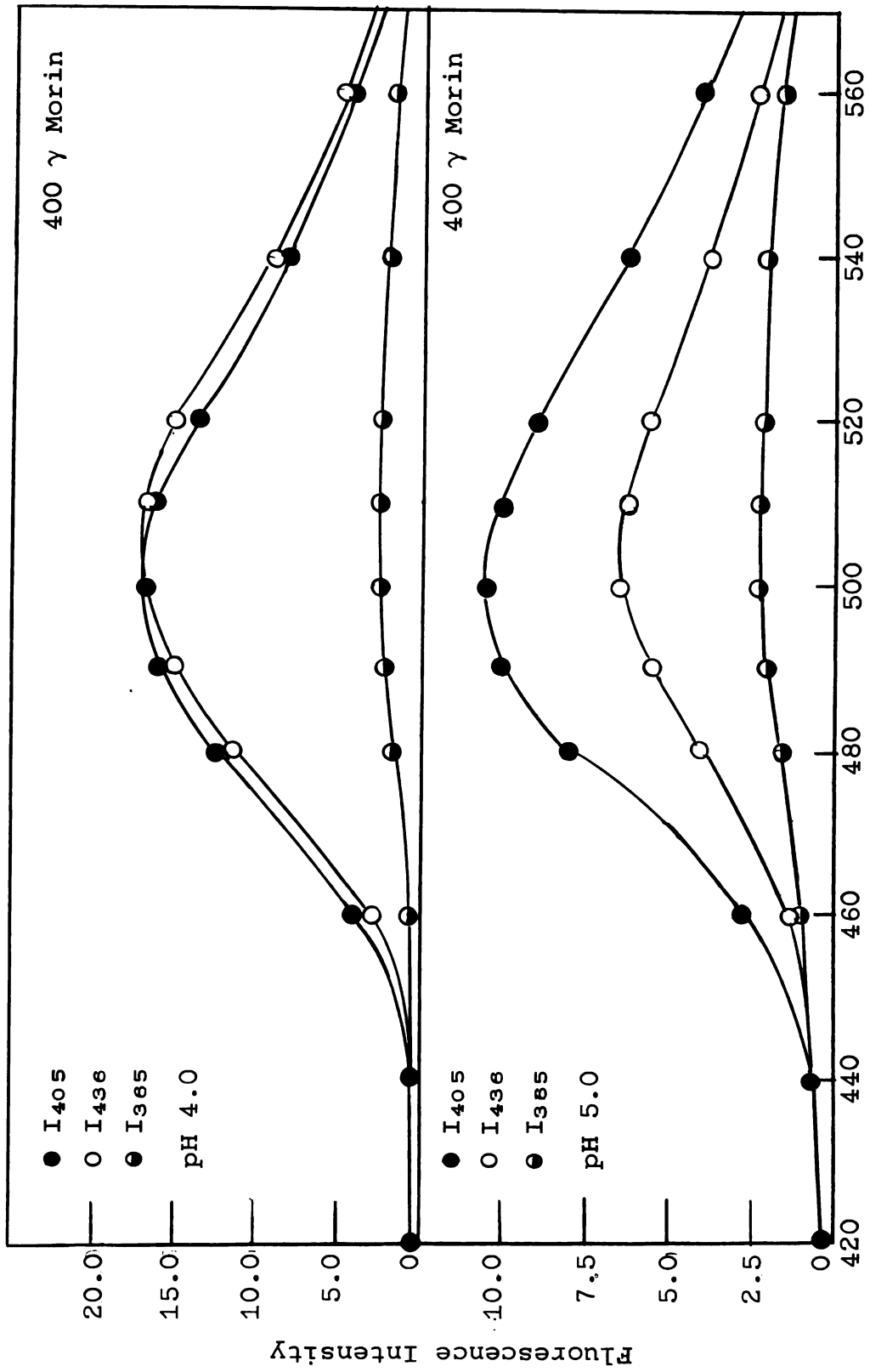

Figure 15. Fluorescence spectra of morin in 50-50 Dw.

Effect of pH on Absorbance

Figures 5-7 show the effect that a change in pH has upon the absorbance of the complex. The absorption maximum of the complex shifts to longer wavelengths with increasing pH. A pH level of 5.0 was selected as the optimum pH for studying the lanthanide (III)-morin complexes as a group.

Nature of the Complex

Isoabsorptive Point

Figures 16-21 show spectrophotometric isoabsorptive points for the six lanthanide (III) complexes at pH 5.0. The formation of only one isoabsorptive point suggests the occurrence of a single reaction (102) 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 concentration of lanthanide (III) ion and morin was 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.

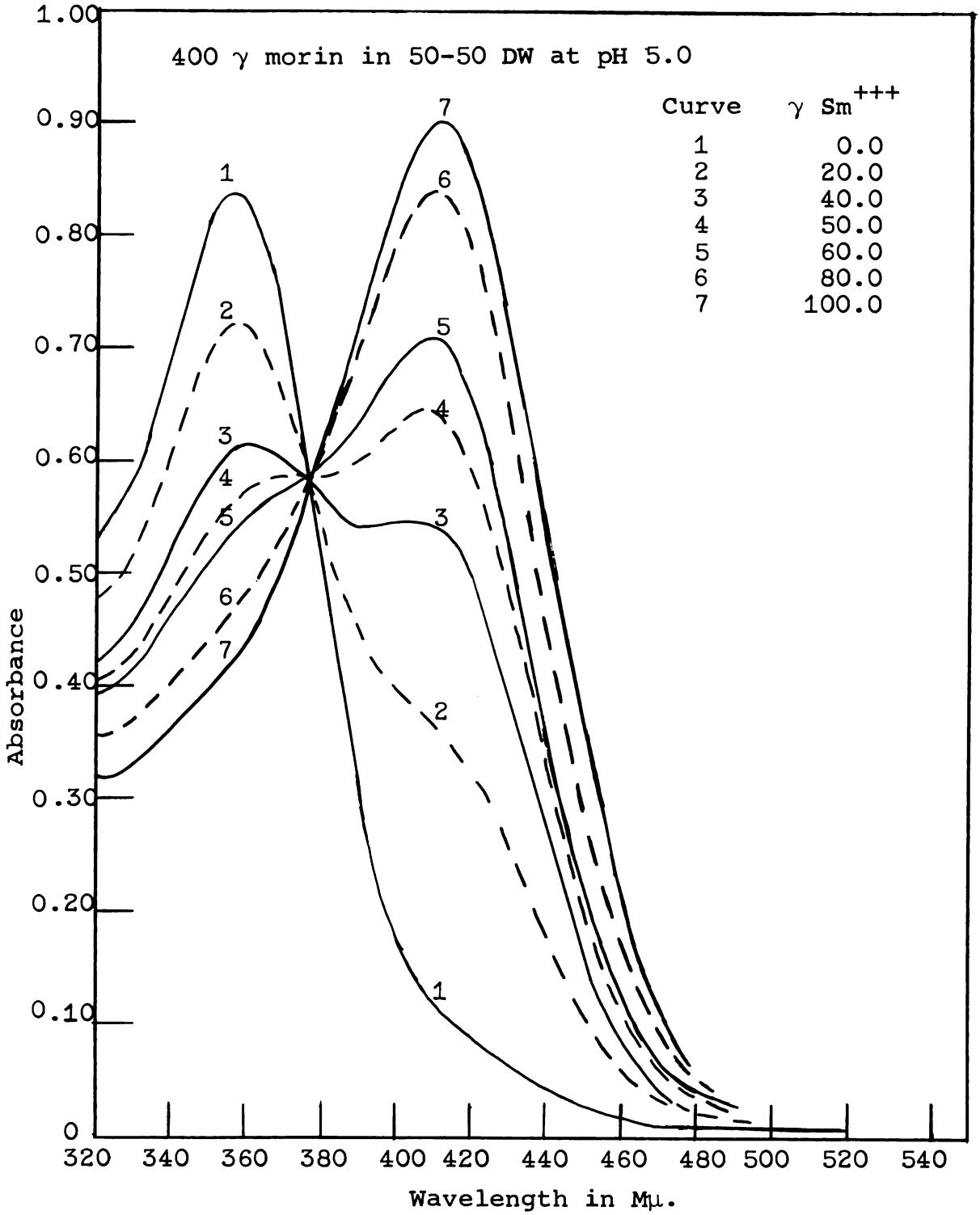

Figure 16. Spectrophotometric isoabsorptive point for the complex of morin with samarium (III).

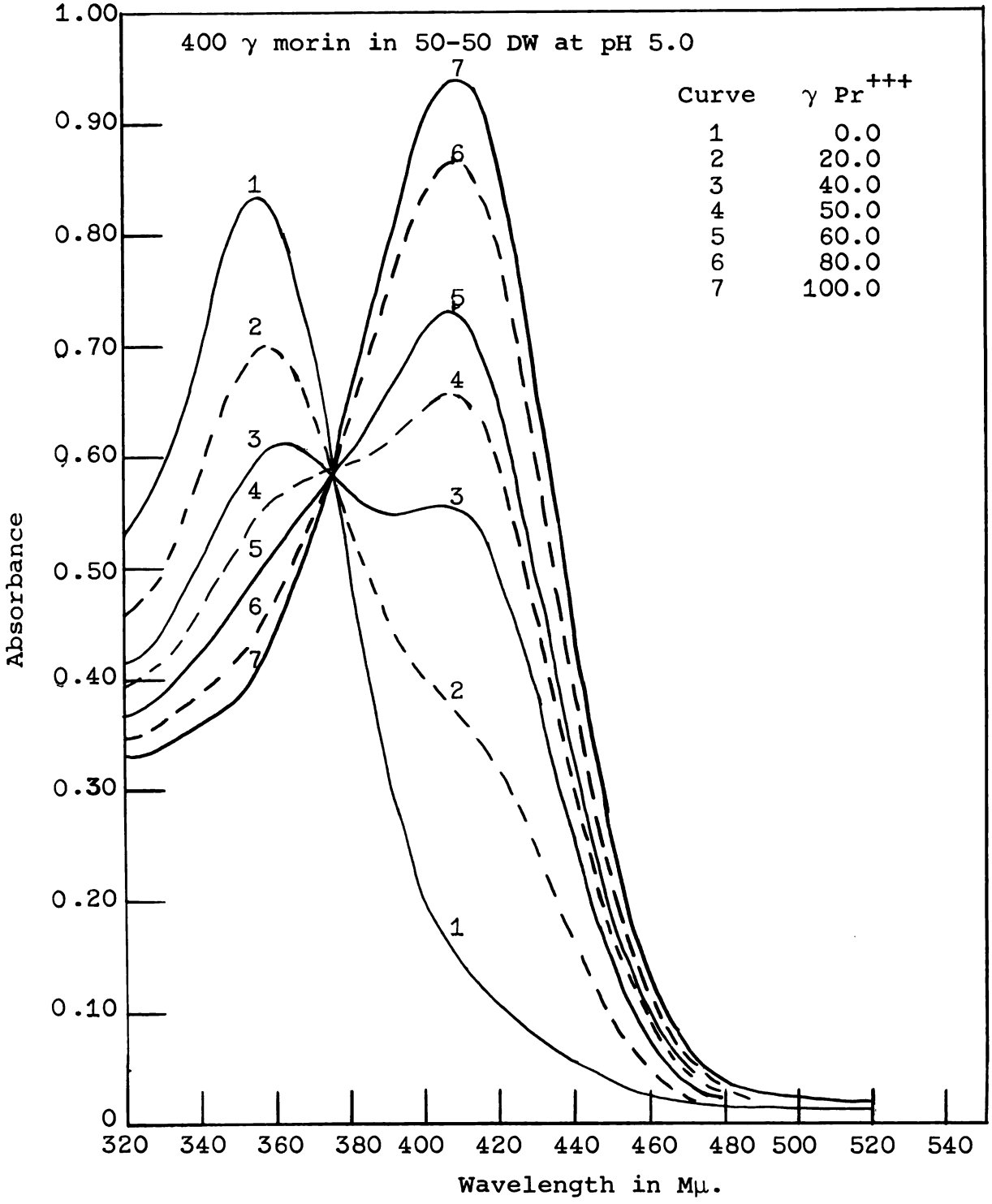

Figure 17. Spectrophotometric isoabsorptive point for the complex of morin with praseodymium (III).

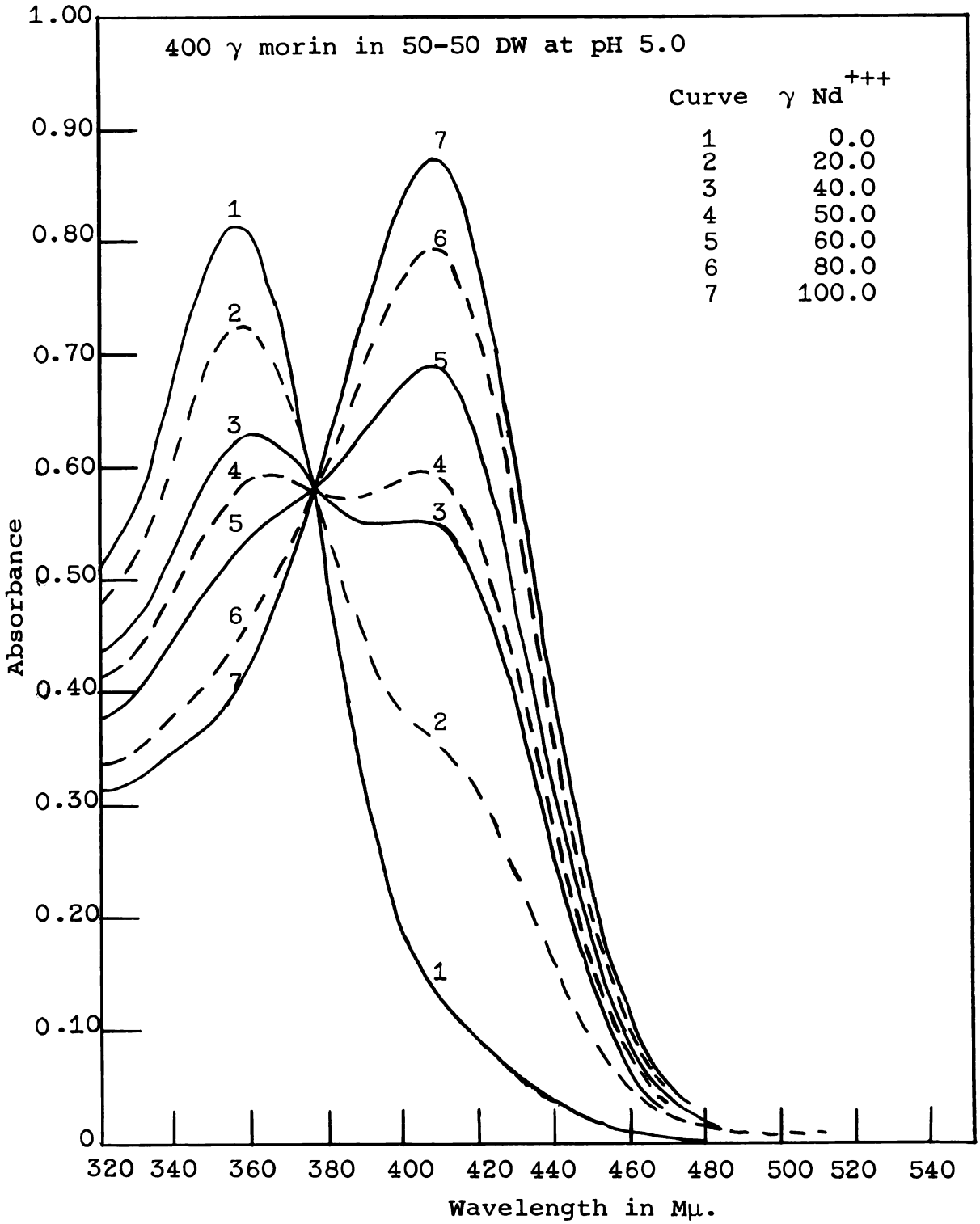

Figure 18. Spectrophotometric isoabsorptive point for the complex of morin with neodymium (III).

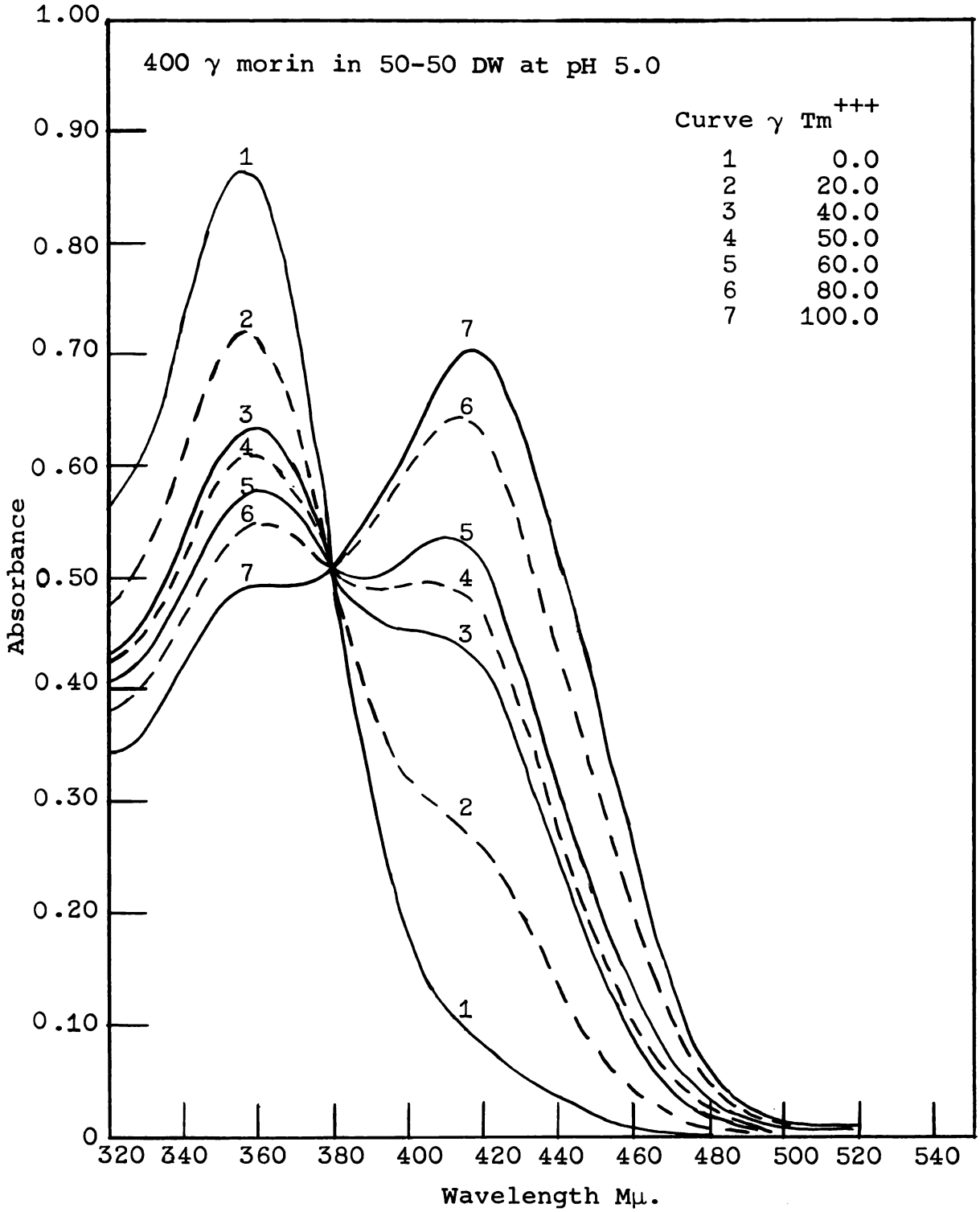

Figure 19. Spectrophotometric isoabsorptive point for the complex of morin with thulium (III).

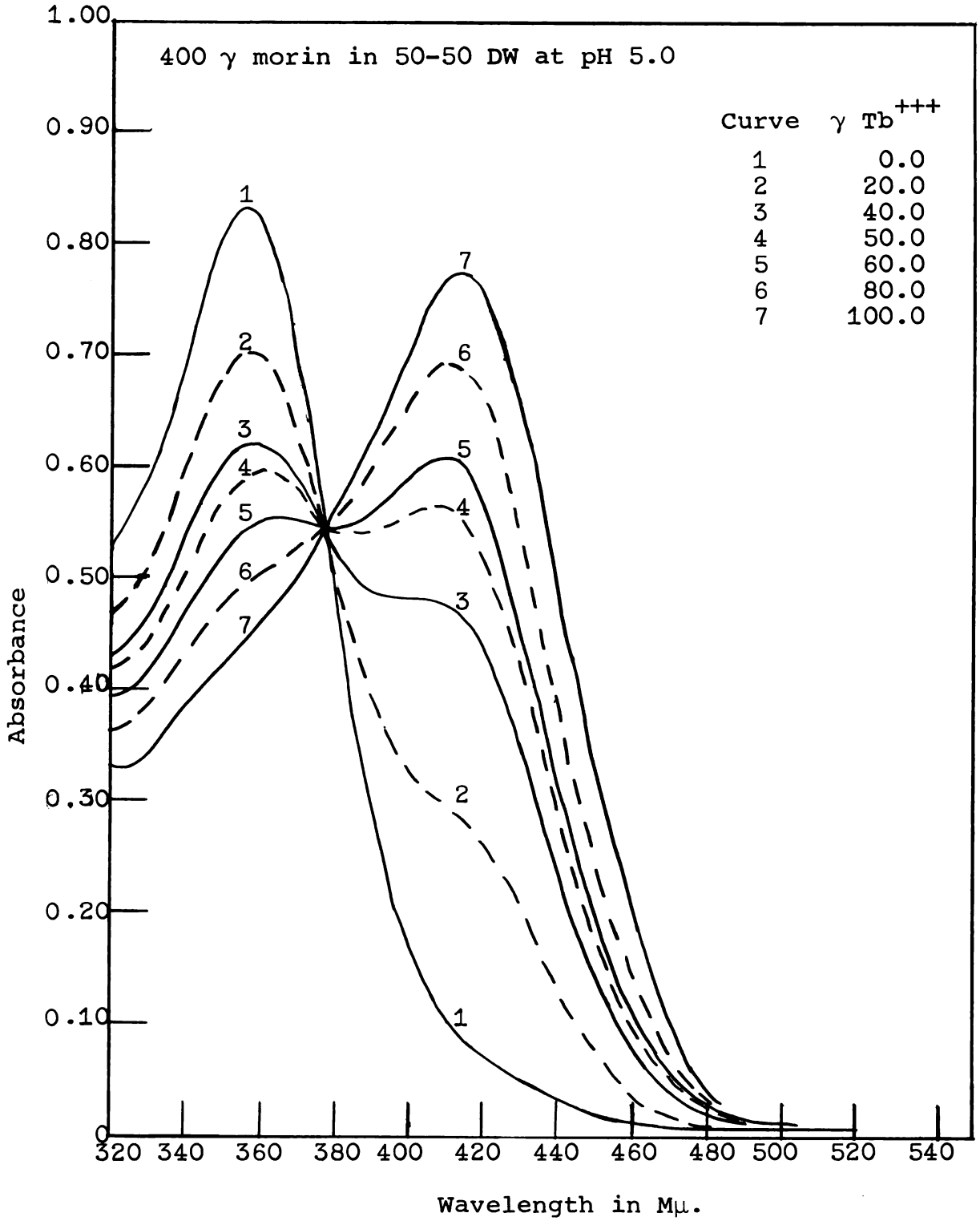

Figure 20. Spectrophotometric isoabsorptive point for the complex of morin with terbium (III).

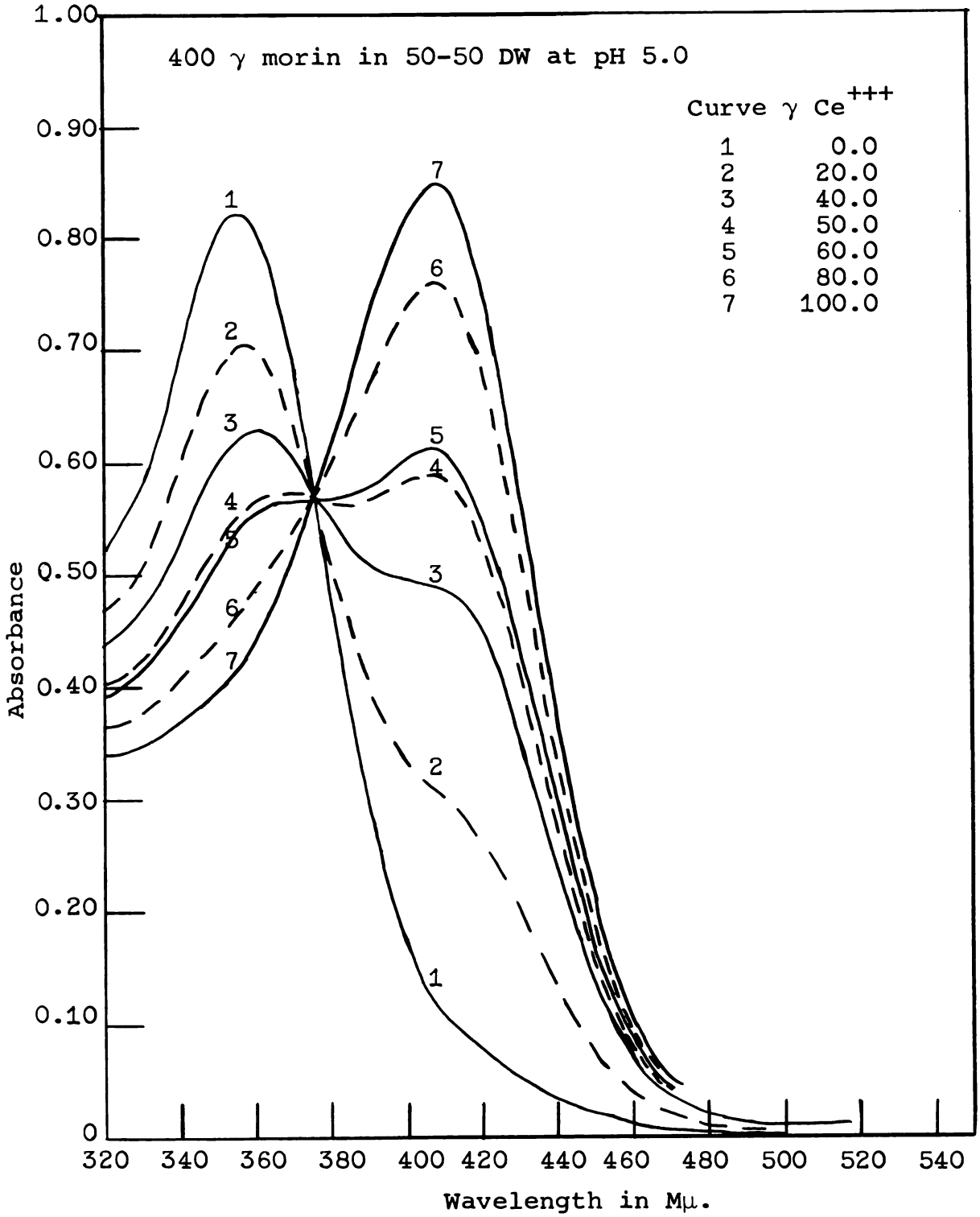

Figure 21. Spectrophotometric isoabsorptive point for the complex of morin with cerium (III).

Both Job (137) and Vosburgh and Cooper (138) have shown that the value of Y at each wavelength is a maximum where the greatest amount of complex is formed. Figures 22-27 show the results obtained when Y is plotted against the mole fraction of lanthanide (III) ion. The maximum, when the absorbance due to the complex is measured, or minimum, when the absorbance due to morin is measured, value of Y appears at a ratio of one mole of lanthanide (III) ion to two moles of morin, indicating a general formula of RM_2^+ for the complex.

Slope Ratio Method

The composition of the complexes was also determined by the slope ratio method of Harvey and Manning (147). Figures 28-32 show that the absorbance at the maximum wavelength for the complex plotted against the moles of morin per liter, curve 1, and against the moles of lanthanide (III) ion per liter, curve 2. 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. The data obtained are summarized in the Appendix (Tables A-VII-A-XI). These data confirm that the general formula of the complex is RM_2^+.

Equilibrium Ratios of the Complexes

The technique used by Milkey and Fletcher (102) in their investigation of the thorium (IV)-morin complex was employed

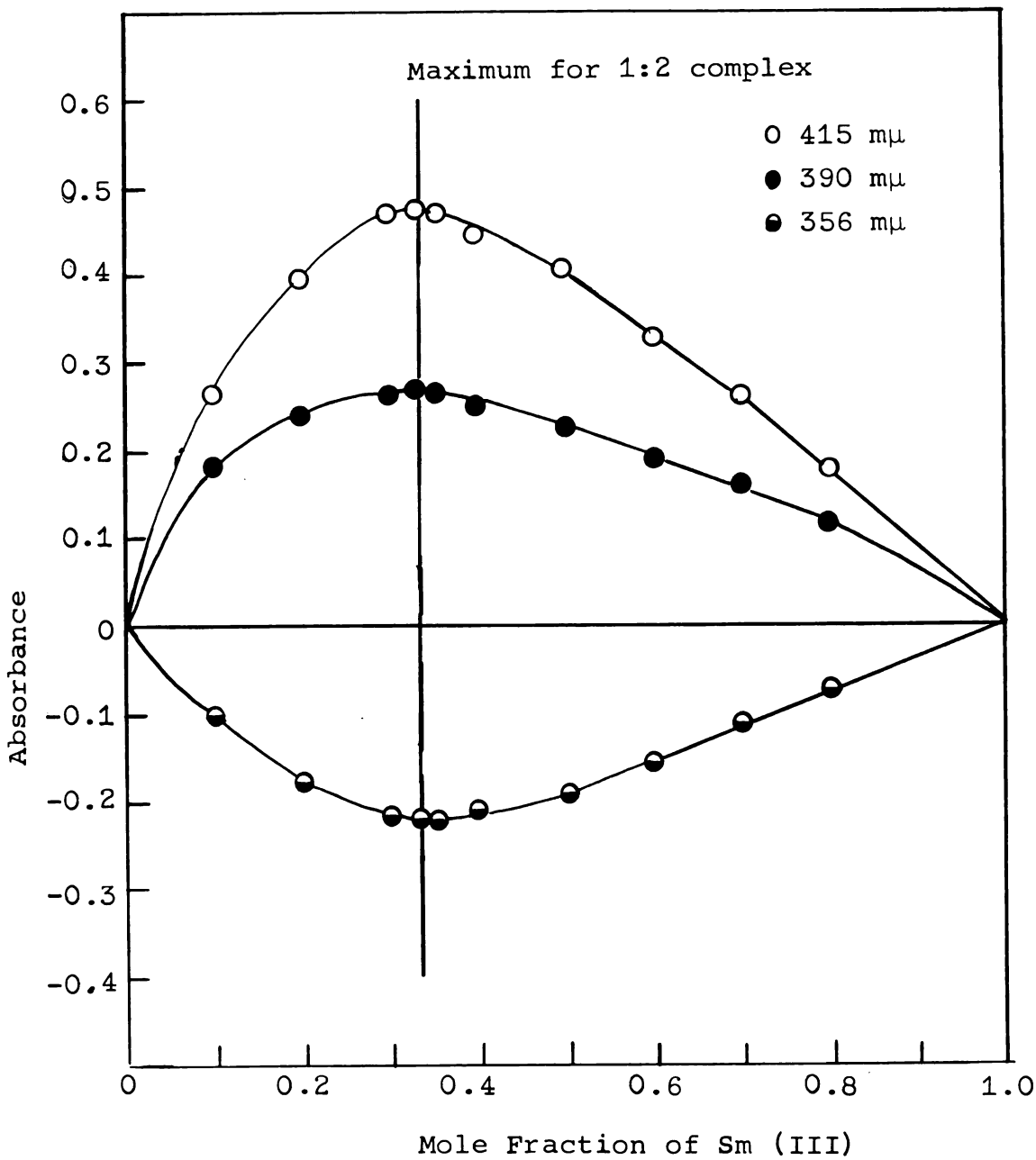

Figure 22. Determination of composition of the samarium (III)-morin complex in 50-50 DW at pH 5.0 by method of continuous variations.

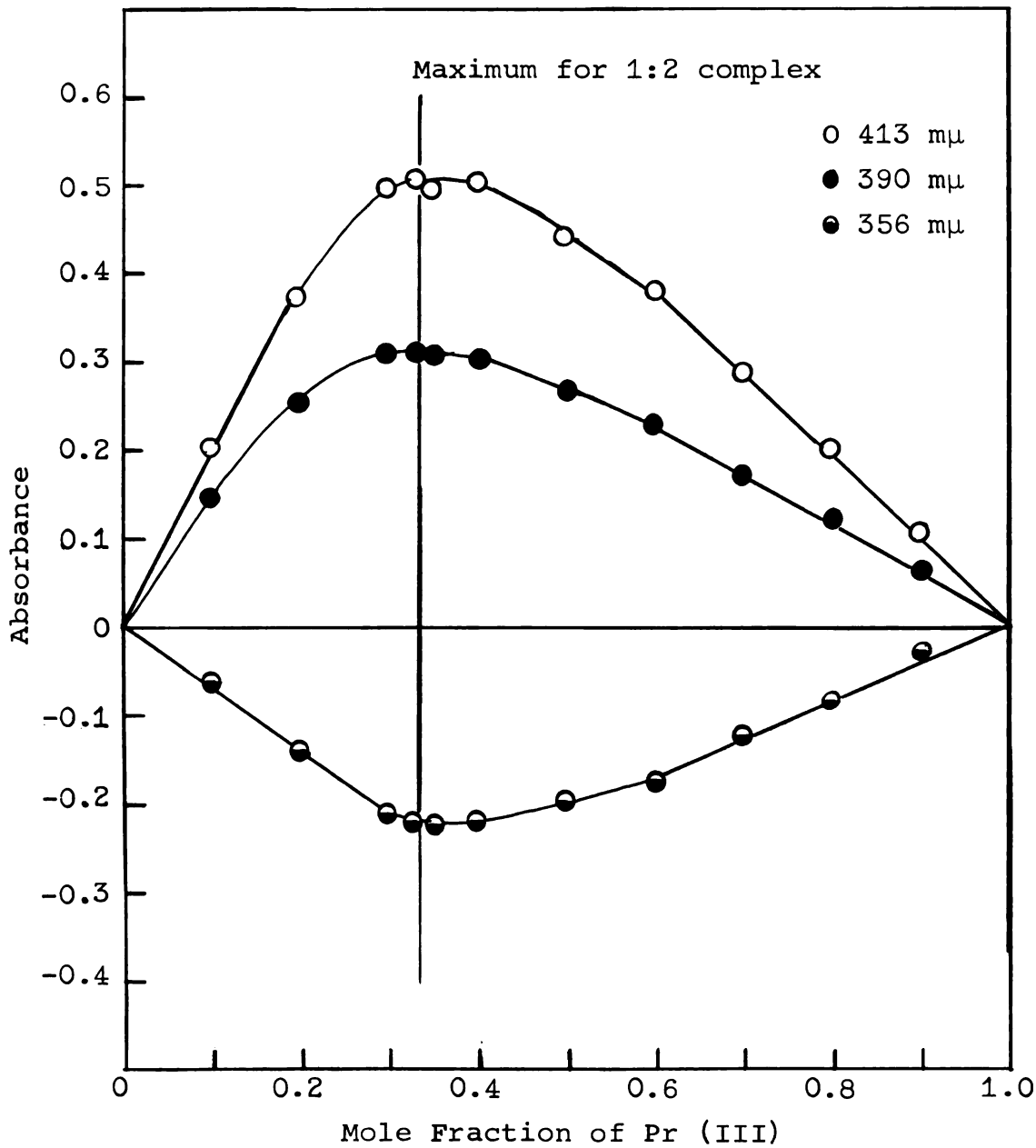

Figure 23. Determination of composition of the praseodymium (III)-morin complex in 50-50 DW at pH 5.0 by method of continuous variations.

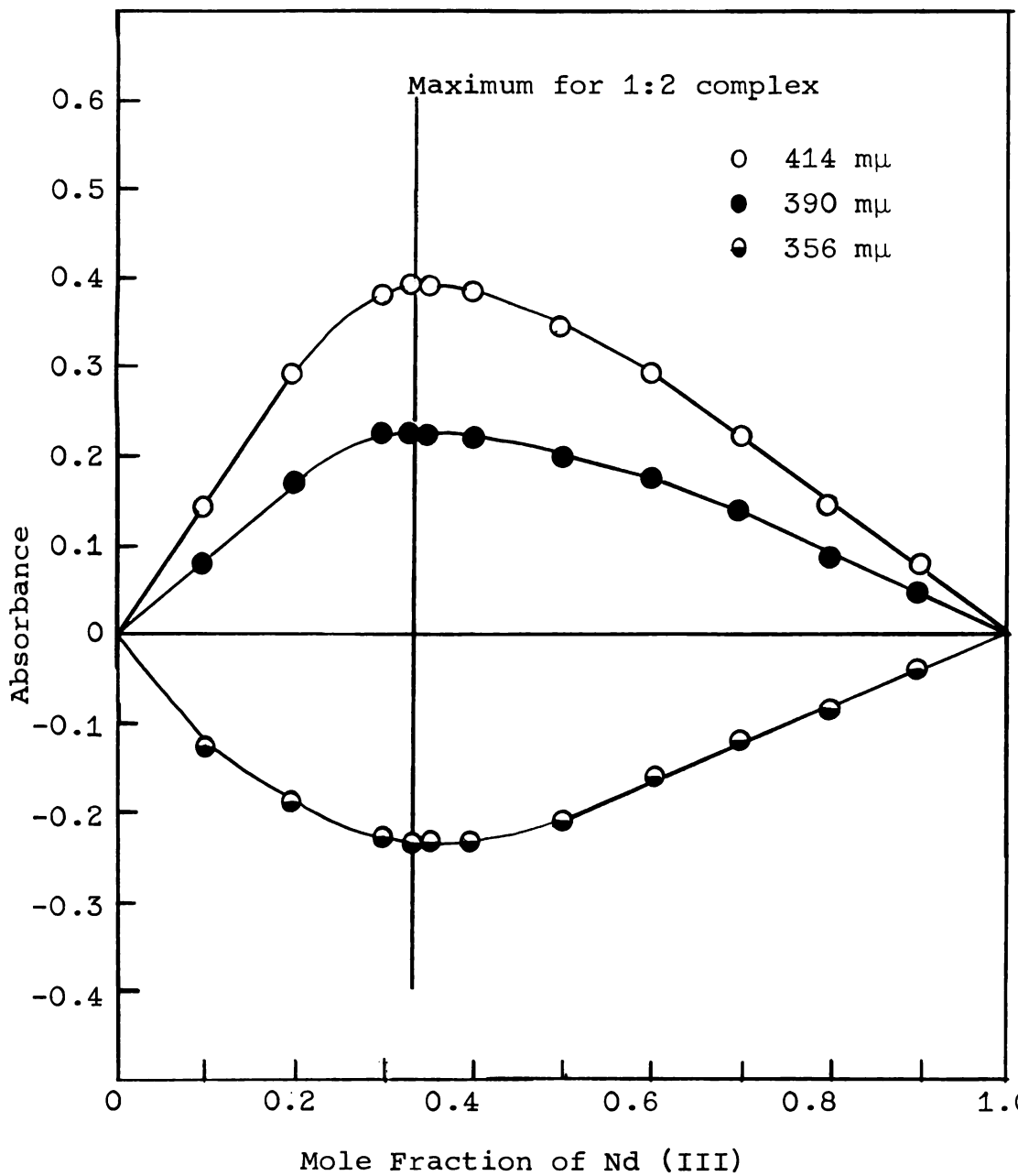

Figure 24. Determination of composition of the neodymium (III)-morin complex in 50-50 DW at pH 5.0 by method of continuous variations.

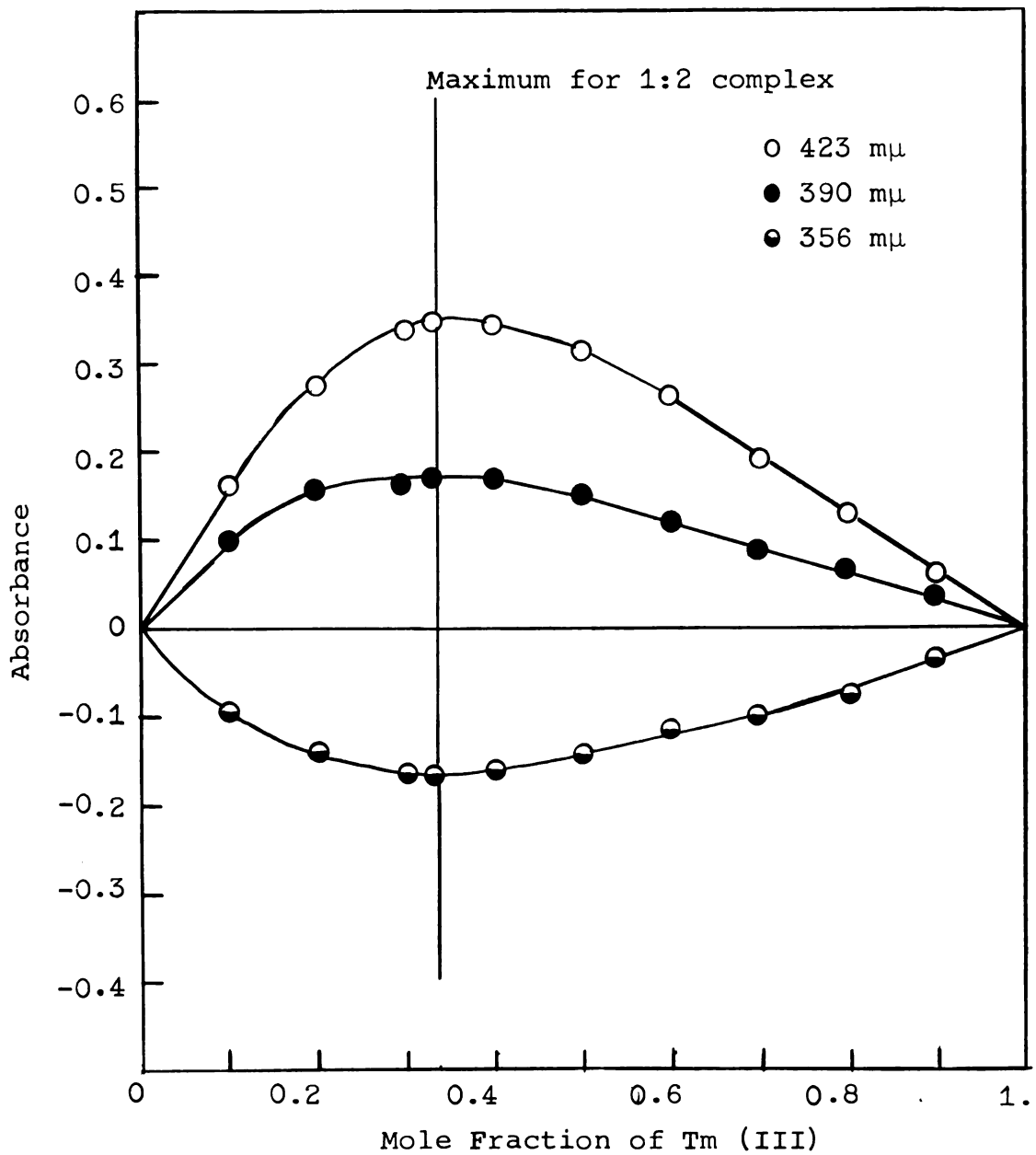

Figure 25. Determination of the composition of the thulium (III)-morin complex in 50-50 DW at pH 5.0 by method of continuous variations.

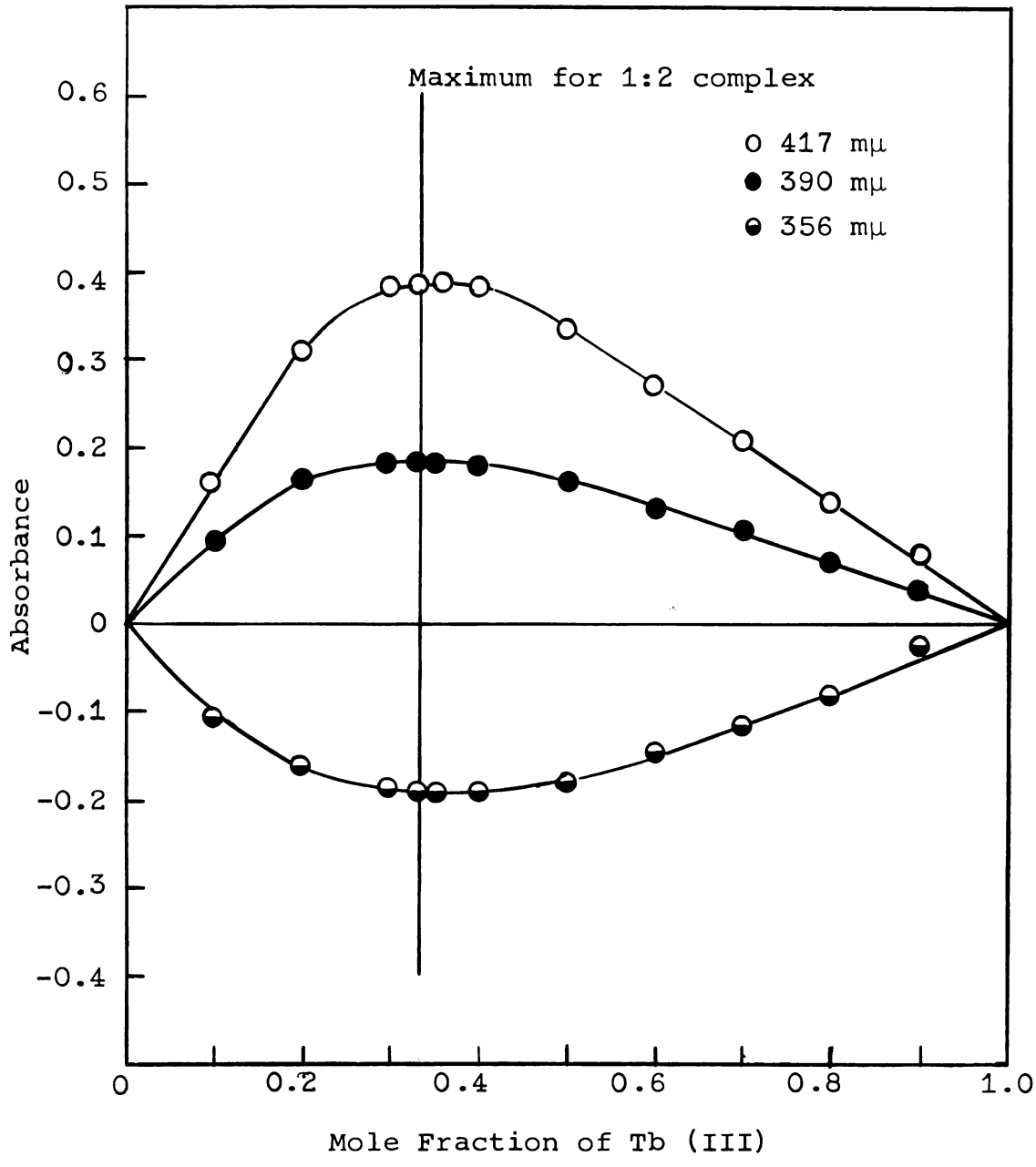

Figure 26. Determination of the composition of the terbium (III)-morin complex in 50-50 DW at pH 5.0 by method of continuous variations.

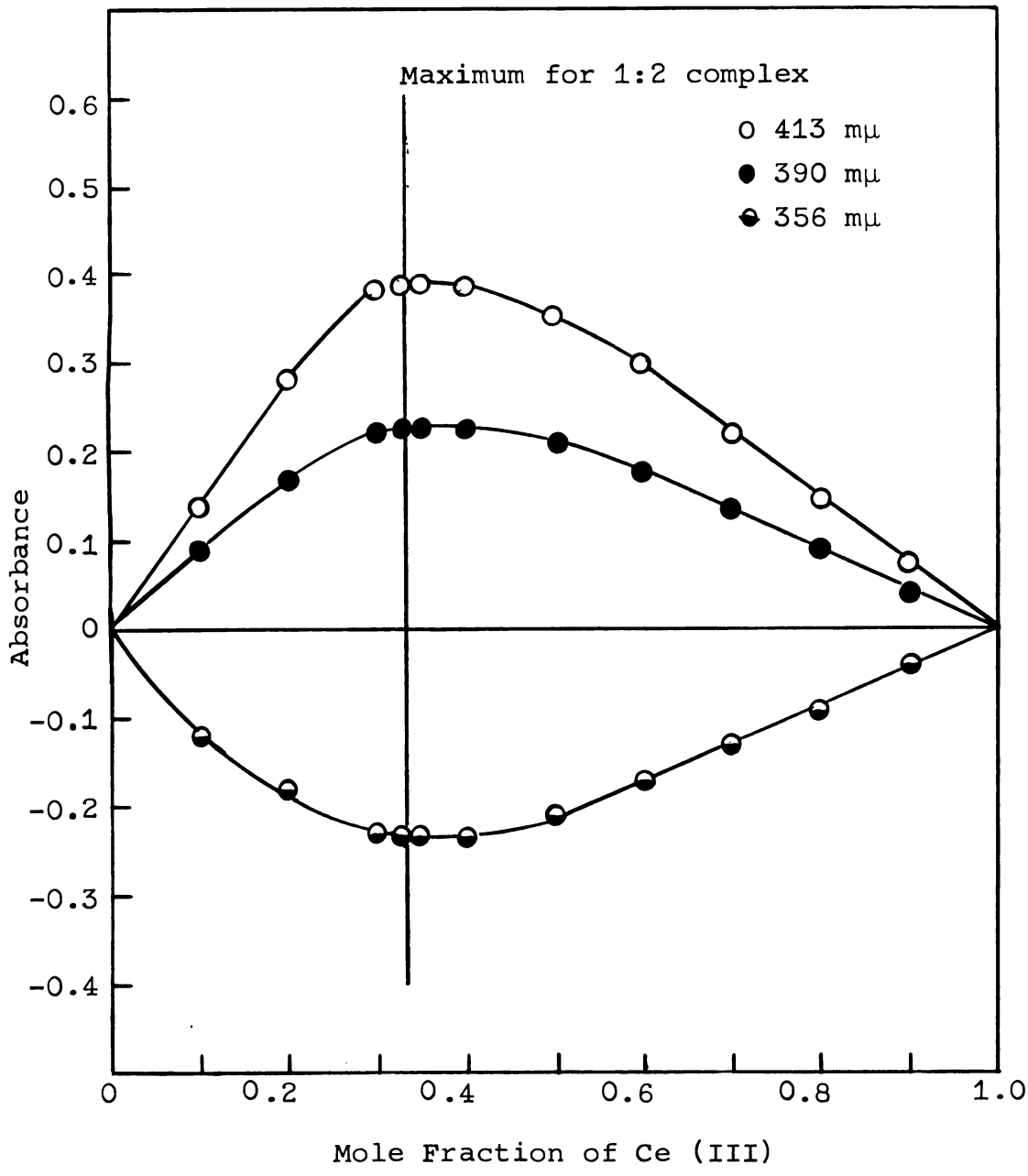

Figure 27. Determination of the composition of the cerium (III)-morin complex in 50-50 DW at pH 5.0 by method of continuous variations.

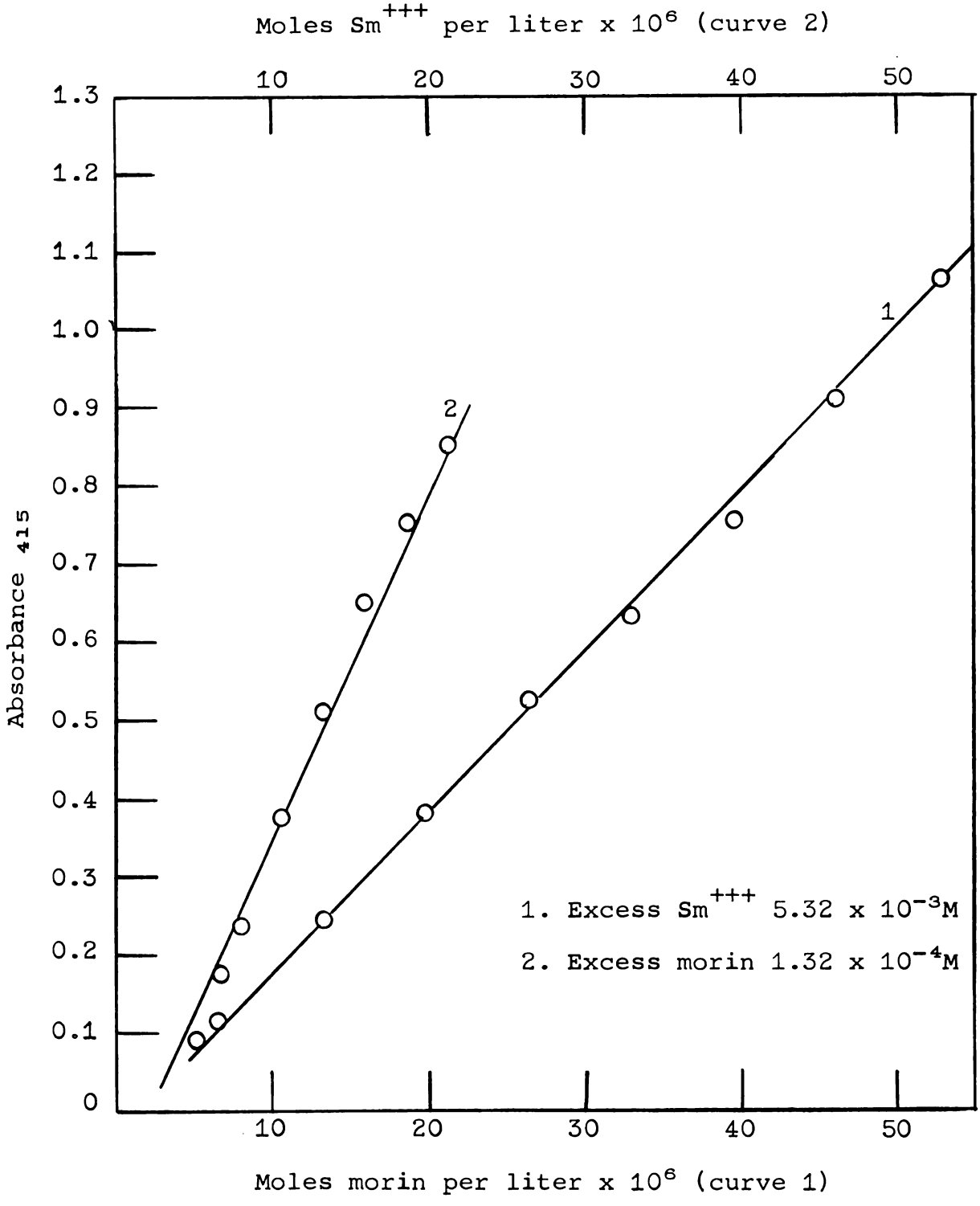

Figure 28. Determination of composition of the samarium (III)-morin complex in 50-50 DW at pH 5.0 by slope-ratio method.

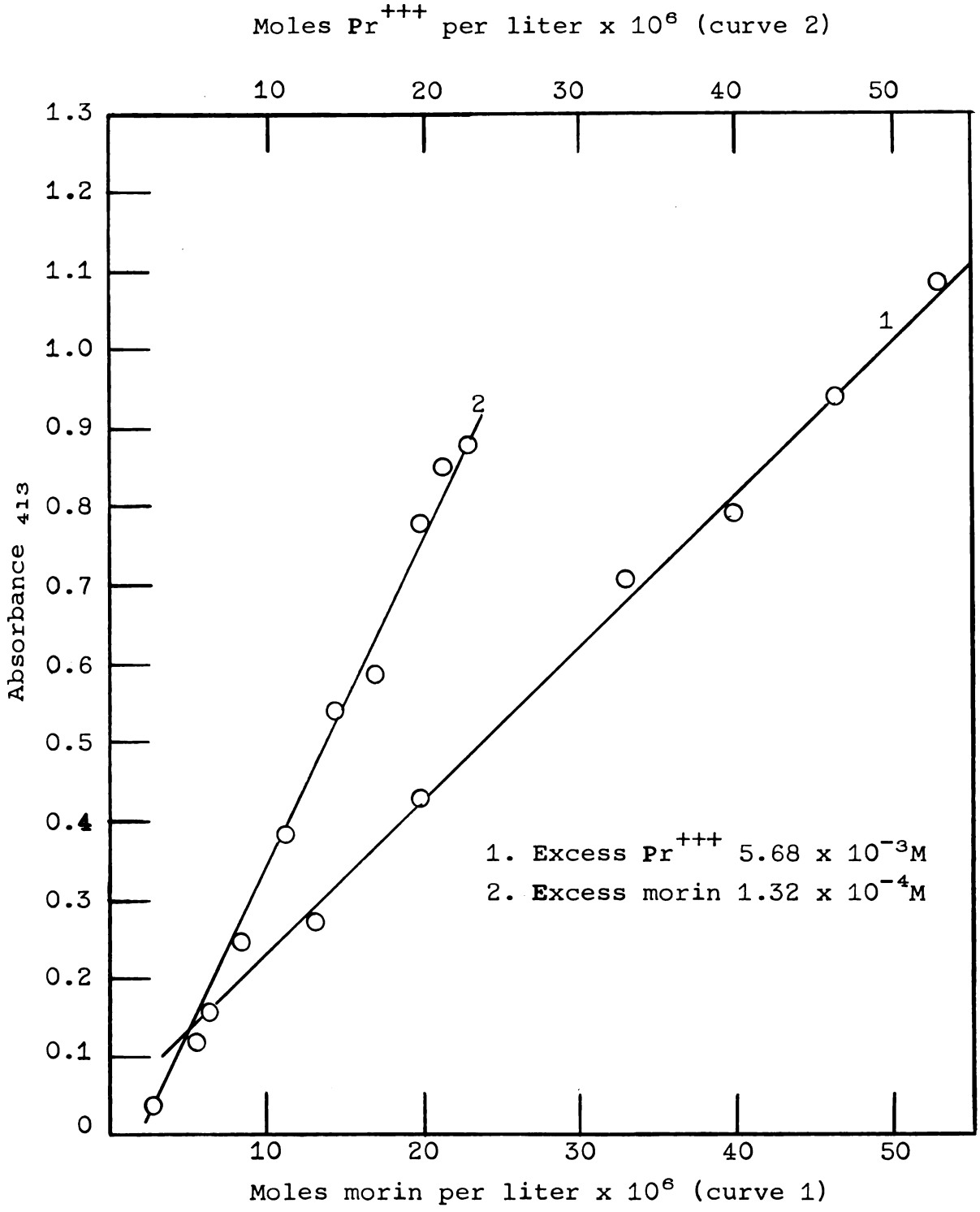

Figure 29. Determination of composition of the praseodymium (III)-morin complex in 50-50 DW at 5.0 by slope-ratio method.

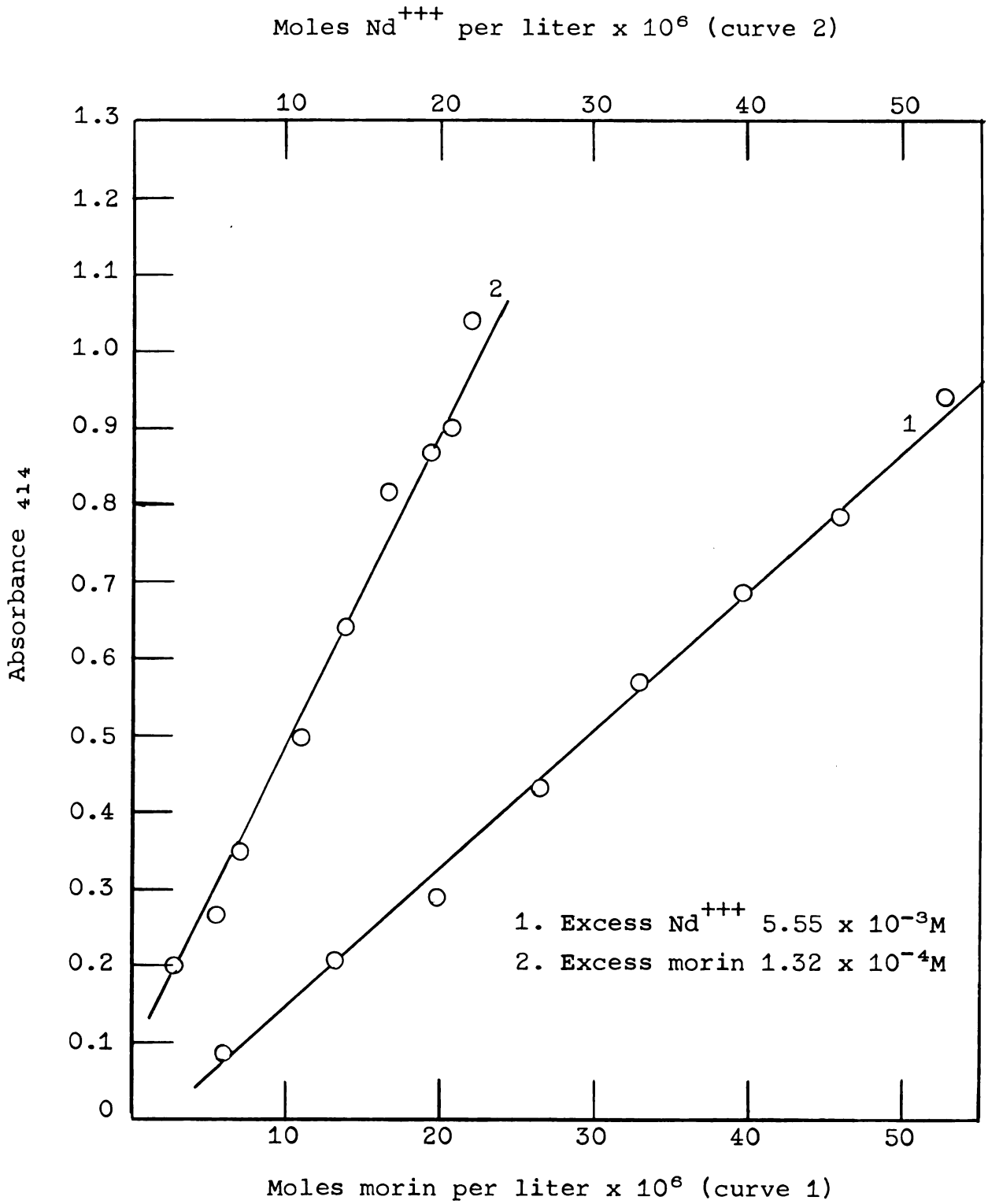

Figure 30. Determination of composition of the neodymium (III)-morin complex in 50-50 DW at pH 5.0 by slope-ratio method.

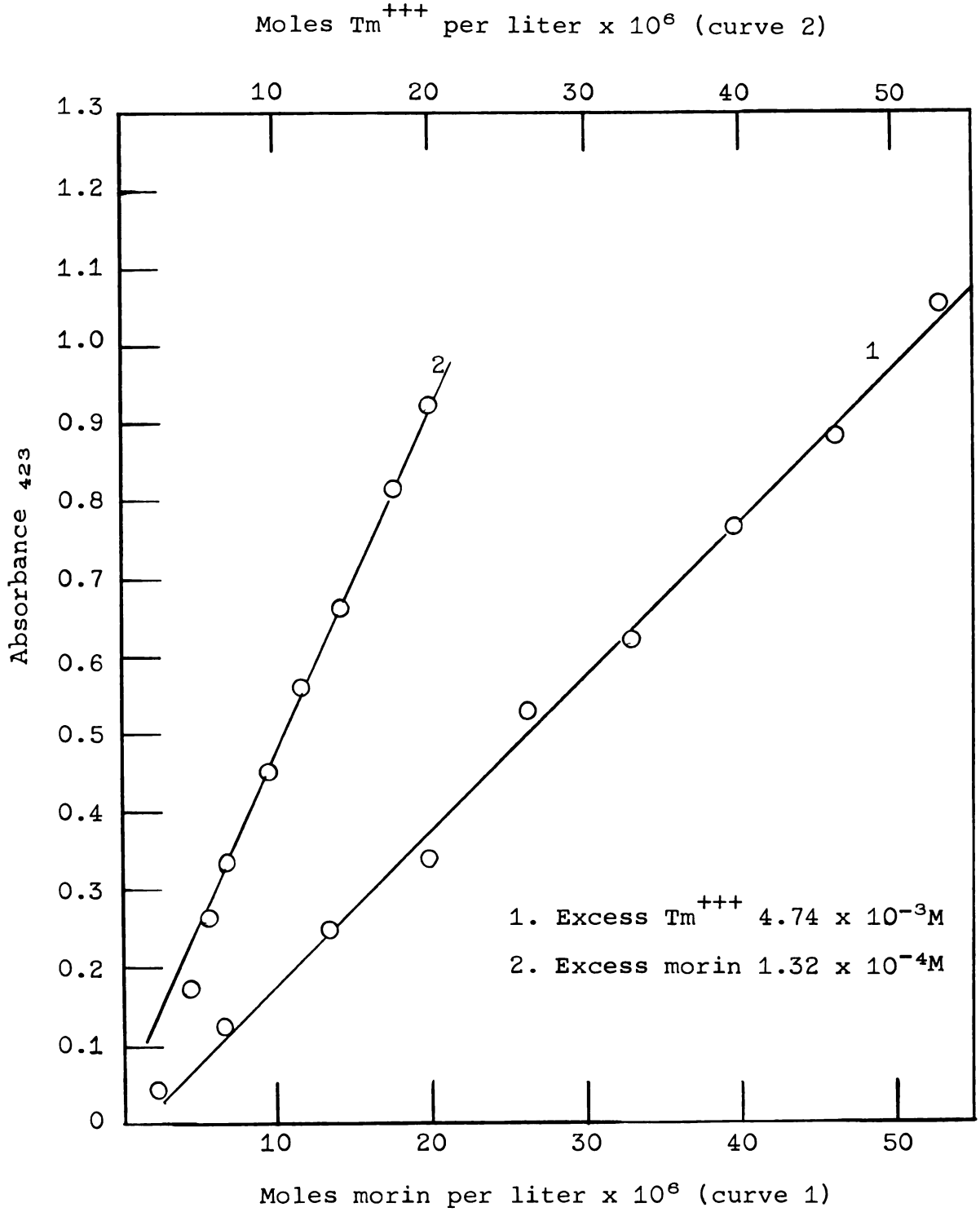

Figure 31. Determination of composition of the thulium (III)-morin complex in 50-50 DW at pH 5.0 by slope-ratio method.

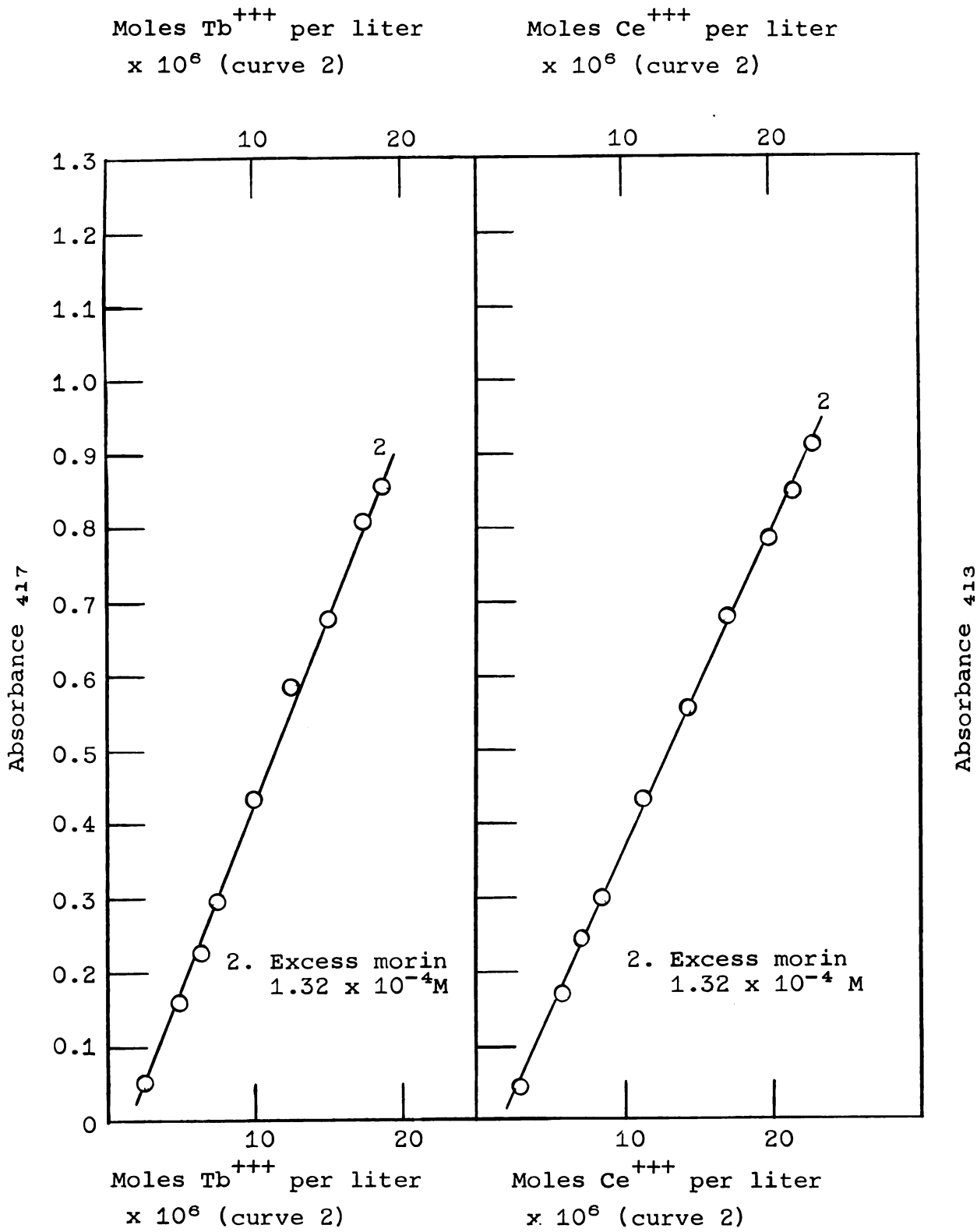

Figure 32. Variation in absorption of terbium (III) and cerium (III)-morin complexes with variation in lanthanide (III) ion concentration in presence of large excess of morin.

to estimate the equilibrium ratio of the various lanthanide (III) ion-morin complexes. The following information was obtained to calculate the equilibrium ratios of the complexes under the conditions of the investigation.

Absorptivity of Morin. Solutions containing morin in the concentration range of approximately 1.0×10^{-5} M. to 5.4×10^{-5} M., and no lanthanide (III) ions were prepared. The solutions were adjusted to pH 5.0 and the absorbances measured. The molar absorptivity was calculated from the absorbance, concentration and cell width. The molar absorptivity of morin at pH 5.0 and 415 mμ. is 2.27×10^{3} L/mole cm., and at pH 5.0 and 423 mμ. is 1.85×10^{3} L/mole cm.

Absorptivity of the Lanthanide (III)-Morin Complex. The molar absorptivities of the praseodymium, neodymium, samarium and thulium complexes were calculated from the slope ratio data obtained in the presence of a large excess of lanthanide (III) ion. The large excess of lanthanide (III) ion insured the complete reaction of all of the morin added to form the complex. By running a blank containing excess lanthanide (III) ion, the contribution of the colored lanthanide (III) ion to the absorbance was determined and subtracted from the total absorbance. Assuming that for each two moles of morin added, one mole of complex is formed, the molar absorptivity of the complex is equal to the absorbance due to the complex divided by one-half of the morin concentration.

The molar absorptivities of the cerium and terbium complexes were calculated from absorbances measured for solutions containing varying amounts of the lanthanide (III) ion in the presence of a large excess of morin. The excess of morin insured complete reaction to the lanthanide (III) ion to form the complex. The observed absorbances are due both to morin and the complex. Assuming that for each mole of lanthanide (III) ion added, one mole of complex is formed, the uncomplexed morin concentration was calculated and the measured absorbance was corrected for the morin absorbance contribution. The molar absorptivity of each complex was calculated from the corrected absorbances.

Concentration of the Components in Solution After Complex Formation. The calculation, as employed by Milkey and Fletcher (102) to determine the concentration of the components in a solution of the complex, was performed using the data obtained in the continuous variations investigation.

In the lanthanide (III)-morin system at the concentration level used in the continuous variations investigation only morin and the complex absorb radiation.

If: X = moles of complex per liter

(MH) = total moles of morin added per liter

(R^{+++}) = total moles of lanthanide (III) ion per liter

Y = moles of uncombined morin per liter

Z = moles of uncombined lanthanide (III) ion per liter

A = absorbance at the desired wavelength of solutions containing the complex

b = path length in cm. (1 cm.)

a_{MH} = molar absorptivity of morin at the desired pH and wavelength

$a_{RM_2}{}^+$ = molar absorptivity of the complex at the desired pH and wavelength

then

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

Solving for X:

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

The concentrations of uncombined morin and lanthanide (III) ion remaining in solution are calculated as follows:

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

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

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

$$R^{+++} + 2\ MH = RM_2{}^+ + 2\ H^+$$

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

$$K'_{eq} = \frac{(RM_2{}^+)\ (H^+)^2}{(R^{+++})\ (MH)^2}$$

where

RM_2^+ = X as calculated above

(R^{+++}) = Z as calculated above

(MH) = Y as calculated above

(H^+) = the hydrogen ion concentration calculated from the pH of the solution

The data for the calculation of the equilibrium ratios are tabulated in the Appendix (Tables A-I - A-VI). The average values for K'_{eq} are 0.83, 4.3, 2.7, 7.9, 0.73 and 2.3 for cerium, neodymium, praseodymium, samarium, terbium and thulium, respectively. The K'_{eq} values are averages over the following approximate ranges of moles of lanthanide (III) ion to morin: for cerium, 1:1 to 1:2.3; for neodymium, 1:1 to 1:4; for praseodymium, 1:1 to 1:9; for samarium, 1:1.5 to 1:2.3; for terbium, 1:0.67 to 1:4 and for thulium, 1:0.1 to 1:9. The values for cerium, neodymium, praseodymium, and samarium are consistent with the values obtained by Fleck (99) for lanthanum, by Weiler (100) for gadolinium and lutetium, and by Van Eenanaam (101) for dysprosium, erbium, europium, holmium and ytterbium. The values for terbium and thulium are anomalous to a uniform trend in the lanthanide (III) series of complexes.

Table 1. K'_{eq} Values and Spectral Properties for Lanthanide (III)-Morin Complexes in 50-50 Dioxane-Water Solutions

Ion	pH	Absorbance $\lambda_{max.}$	Fluorescence $\lambda_{excit.}$	Fluorescence $\lambda_{fluor.}$	Intensity	K'_{eq}	Reference
La	5.5	410	365	505-10	strong	0.6	99
Ce	5.0	413	413	505-10	weak	0.83	present study
Pr	5.0	413	413	505-510	weak	2.7	present study
Nd	5.0	414	414	505-10	weak	4.3	present study
Sm	5.0	415	415	505-10	weak	7.9	present study
Eu	5.5	408	---	---	---	15.1	101
	5.0		405	505-10	very weak	---	101
Gd	4.25	410	365	505-10	strong	14.8	100
Tb	5.0	417	417	505-10	weak	0.73	present study
Dy	5.0	414	405	505-10	very weak	19.4	101
Ho	5.0	419	405	505-10	weak	20.9	101
Er	5.0	414	405	505-10	weak	24.6	101
Tm	5.0	423	423	505-10	weak	2.3	present study
Yb	5.0	419	405	505-10	weak	31.5	101
Lu	4.25	410	365	505-10	strong	32.9	100

SUMMARY AND CONCLUSIONS

A spectrophotometric and spectrofluorometric investigation of the complexes of morin with cerium (III), neodymium (III), praseodymium (III), samarium (III), terbium (III) and thulium (III) in 50-50 DW solution was completed.

The absorption band peak of morin occurs at 356 mμ., while the complex absorption band peaks for cerium and praseodymium, neodymium, samarium, terbium, and thulium occur at 413, 414, 415, 417, and 423 mμ., respectively.

The complexes fluoresce only slightly more than morin when exposed to incident radiation of 365, 436 mμ. or there absorption maximum wavelength. The complexes of lanthanum, gadolinium and lutetium fluoresce significantly under the same conditions.

The pH of the solution affects the absorbance of the complexes. A pH level of 5.0 was selected as the optimum pH for investigating this series of complexes. The absorption maxima shift slightly to longer wavelengths with increasing pH.

In the absorption spectra of each of the complexes, a single isoabsorptive point exists. The isoabsorptive point occurs near 377 mμ. The existence of an isoabsorptive point suggests that a single complex is formed.

Job's method of continuous variations (137) and Harvey and Manning's slope ratio method (147) 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 calculated in the manner proposed by Milkey and Fletcher (102). The K'_{eq} values for the cerium, neodymium, praseodymium, samarium, terbium and thulium complexes with morin in 50-50 DW at 25°C are 0.83, 4.3, 2.7, 7.9, 0.73 and 2.3, respectively.

The absorbances for the complexes change linearly with changing lanthanide (III) concentration over the approximate concentration range, 0 to 2.3×10^{-5} M., in the presence of excess morin, 1.32×10^{-4} M.

The formation constants for lanthanide (III)-EDTA (151) complexes increase regularly from lanthanum to lutetium. In the present study, the concentration quotients for the terbium and thulium-morin complexes are anomalous. No explanation for this departure can be offered at the present time but the reaction between these two lanthanide ions and morin should be reinvestigated in greater detail.

Furthermore, the acid dissociation constant for morin should be evaluated so that the formation constant for the reaction

$$R^{+++} + 2\,M^{-} \rightleftharpoons RM_2^{+}$$

can be calculated.

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APPENDIX

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

Trial	Total Sm^{+++} Added M/l x 10^6	Total MH Added M/l x 10^6	H^+ M/l x 10^6	Z M/l x 10^6	Y M/l x 10^6	$Sm(M)_2^+$ M/l x 10^6	A_{415}	K_{eq}
1.	5.32	47.9	10.0	---	32.1	7.91	0.375	---
2.	10.6	42.6	10.0	---	19.0	11.8	0.495	---
3.	16.0	37.2	10.0	2.0	9.2	14.0	0.555	8.3
4.	17.6	35.4	10.0	3.4	7.0	14.2	0.560	8.5
5.	18.6	34.6	10.0	4.6	6.6	14.0	0.550	7.0
6.	21.3	31.9	10.0	8.2	5.7	13.1	0.515	4.9*
7.	26.6	26.6	10.0	14.6	2.6	12.0	0.465	12.2*
8.	31.9	21.3	10.0	22.1	1.6	9.85	0.380	17.4*
9.	37.2	16.0	10.0	29.5	0.6	7.69	0.295	72.4*
10.	42.6	10.6	10.0	37.2	---	5.38	0.205	---

MH = Morin
Z = Moles of uncombined samarium (III) per liter
Y = Moles of uncombined morin per liter
Absorbance values and data were obtained from solutions used in the continuous variations study.
* Not included in the calculation of the average value.

Table A-II. Estimated Equilibrium Ratio, K'_{eq}, Values of the Praseodymium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Total Added Pr^{+++} M/l x 10^6	Total MH Added M/l x 10^6	H^+ M/l x 10^6	Z M/l x 10^6	Y M/l x 10^6	$Pr(M)_2^+$ M/l x 10^6	A_{413}	K_{eq}
1.	5.68	51.1	10.0	0.2	40.2	5.47	0.315	1.7
2.	11.4	45.4	10.0	1.0	24.6	10.4	0.480	1.7
3.	17.0	39.7	10.0	3.4	12.5	13.6	0.585	2.6
4.	18.7	37.8	10.0	4.8	10.0	13.9	0.590	2.9
5.	19.9	36.9	10.0	6.4	9.9	13.5	0.575	2.2
6.	22.7	34.1	10.0	8.9	6.5	13.8	0.580	3.7
7.	28.4	28.4	10.0	16.3	4.2	12.1	0.505	4.2
8.	34.1	22.7	10.0	23.7	1.9	10.4	0.430	12.2*
9.	39.7	17.0	10.0	32.0	1.5	7.74	0.320	10.8*
10.	45.4	11.4	10.0	40.0	0.4	5.48	0.225	85.6*
11.	51.1	5.68	10.0	48.3	0.1	2.81	0.115	582*

MH = Morin
Z = Moles of uncombined praseodymium (III) per liter
Y = Moles of uncombined morin per liter
Absorbance values and data were obtained from solutions used in the continuous variations study.
* Not included in the calculation of the average value.

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

Trial	Total Nd^{+++} Added M/l x 10^6	Total MH Added M/l x 10^6	H^+ M/l x 10^6	Z M/l x 10^6	Y M/l x 10^6	$Nd(M)_2^+$ M/l x 10^6	A_{414}	K'_{eq}
1.	5.55	49.9	10.0	0.4	39.6	5.14	0.255	0.8*
2.	11.1	44.4	10.0	0.6	23.4	10.5	0.390	3.2
3.	16.6	38.8	10.0	2.7	11.0	13.9	0.470	4.3
4.	18.3	37.2	10.0	3.3	6.9	15.0	0.475	9.5*
5.	19.4	36.1	10.0	5.4	8.1	14.0	0.470	4.0
6.	22.2	33.3	10.0	8.3	5.5	13.9	0.460	5.5
7.	27.7	27.7	10.0	15.3	2.9	12.4	0.405	9.6*
8.	33.3	22.2	10.0	22.6	0.8	10.7	0.345	74*
9.	38.8	16.6	10.0	30.5	0.0	8.30	0.265	---
10.	44.4	11.1	10.0	39.2	0.6	5.25	0.170	37*
11.	49.9	5.55	10.0	47.1	---	2.81	0.090	---

MH = Morin
Z = Moles of uncombined neodymium (III) per liter
Y = Moles of uncombined morin per liter
Absorbances and data were obtained from solutions used in the continuous variations study.
*Not included in the calculation of the average value.

Table A-IV. Estimated Equilibrium Ratio, K'_{eq}, Values of the Thulium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Total Tm^{+++} Added M/l x 10^6	Total MH Added M/l x 10^6	H^+ M/l x 10^6	Z M/l x 10^6	Y M/l x 10^6	$Tm(M)_2^+$ M/l x 10^6	A_{423}	K'_{eq}
1.	4.74	42.6	10.0	---	32.5	5.06	0.255	---
2.	9.47	37.9	10.0	1.28	21.5	8.19	0.355	1.4
3.	14.2	33.1	10.0	4.0	12.7	10.2	0.415	1.6
4.	15.6	31.5	10.0	5.2	10.7	10.4	0.420	1.7
5.	18.9	28.4	10.0	8.6	7.8	10.3	0.410	2.0
6.	23.7	23.7	10.0	14.3	5.0	9.37	0.370	2.6
7.	28.4	18.9	10.0	20.6	3.4	7.76	0.305	3.3
8.	33.1	14.2	10.0	27.5	3.1	5.57	0.220	2.1
9.	37.9	9.47	10.0	34.1	1.9	3.81	0.150	3.1
10.	42.6	4.74	10.0	40.8	1.2	1.76	0.070	3.0

MH = Morin
Z = Moles of uncombined thulium (III) per liter
Y = Moles of uncombined morin per liter
Absorbance values and data were obtained from solutions used in the continuous variations study.

Table A-V. Estimated Equilibrium Ratio, K'_{eq}, Values of the Terbium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Total Tb^{+++} Added M/l x 10^6	Total MH Added M/l x 10^6	H^+ M/l x 10^6	Z M/l x 10^6	Y M/l x 10^6	$Tb(M)_2^+$ M/l x 10^6	A_{417}	K'_{eq}
1.	5.03	45.3	10.0	0.9	37.0	4.16	0.265	0.34*
2.	10.1	40.3	10.0	2.2	24.5	7.92	0.400	0.60
3.	15.1	35.2	10.0	5.3	15.7	9.76	0.460	0.75
4.	16.6	33.5	10.0	6.7	13.8	9.86	0.460	0.77
5.	17.6	32.7	10.0	7.7	12.9	9.90	0.460	0.77
6.	20.1	30.2	10.0	10.3	11.6	9.79	0.450	0.71
7.	25.2	25.5	10.0	16.7	8.1	8.54	0.390	0.78
8.	30.2	20.1	10.0	24.3	6.3	6.91	0.315	0.72
9.	35.2	15.1	10.0	29.8	4.3	5.41	0.245	0.98*
10.	40.3	10.1	10.0	36.8	3.1	3.52	0.160	1.0 *
11.	45.3	5.03	10.0	43.4	1.0	2.02	0.090	4.7 *

MH = Morin
Z = Moles of uncombined terbium (III) per liter
Y = Moles of uncombined morin per liter
Absorbances values and data were obtained from solutions used in the continuous variations study.
*Not included in the calculation of the average value.

Table A-VI. Estimated Equilibrium Ratio, K'_{eq}, Values of the Cerium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Total Ce^{+++} Added M/l x 10^6	Total MH Added M/l x 10^6	H^+ M/l x 10^6	Z M/l x 10^6	Y M/l x 10^6	$Ce(M)_2^+$ M/l x 10^6	A_{413}	K'_{eq}
1.	5.71	51.4	10.0	1.6	43.1	4.13	0.255	0.14*
2.	11.4	45.7	10.0	2.8	28.6	8.56	0.390	0.37*
3.	17.1	40.0	10.0	5.6	17.0	11.5	0.475	0.71
4.	18.8	38.0	10.0	7.2	14.8	11.6	0.475	0.74
5.	20.0	37.1	10.0	8.3	13.7	11.7	0.475	0.75
6.	22.8	34.3	10.0	11.2	11.1	11.6	0.465	0.84
7.	28.5	28.5	10.0	17.9	7.3	10.6	0.420	1.1
8.	34.3	22.8	10.0	25.4	5.0	8.91	0.350	1.4 *
9.	40.0	17.1	10.0	33.4	3.9	6.61	0.260	1.3 *
10.	45.7	11.4	10.0	41.2	2.5	4.46	0.175	1.7 *
11.	51.4	5.71	10.0	49.3	1.4	2.15	0.085	2.2 *

MH = Morin
Z = Moles of uncombined cerium (III) per liter
Y = Moles of uncombined morin per liter
Absorbance values and data were obtained from solutions used in the continuous variations study.
*Not included in the calculation of the average value.

Table A-VII. Slope Ratio Data for Samarium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Excess Sm(III), 5.32×10^{-3} M (Morin) M/1 x 10^6	pH	A_{415}*	Trial	Excess Morin, 1.32×10^{-4} M (Sm^{+++}) M/1 x 10^6	pH	A_{415}**
1.	6.62	5.00	0.115	1.	5.32	5.00	0.089
2.	13.23	5.00	0.245	2.	6.65	5.00	0.175
3.	19.85	5.00	0.380	3.	7.98	5.00	0.236
4.	26.47	5.00	0.525	4.	10.64	5.00	0.373
5.	33.08	5.00	0.635	5.	13.30	5.00	0.511
6.	39.70	5.00	0.755	6.	15.96	5.00	0.653
7.	46.32	5.00	0.910	7.	18.62	5.00	0.755
8.	52.94	5.00	1.065	8.	21.28	5.00	0.847

*Absorbance corrected for excess Sm(III) contribution
**Absorbance corrected for excess morin contribution
From Figure 28, slope of line 1, 2.078×10^4; slope of line 2, 4.471×10^4.
The ratio of the slopes is 1.00/2.15

Table A-VIII. Slope Ratio Data for Praseodymium (III)-Morin Complex in 50-50 DW at 25°C

Excess Pr(III), 5.68×10^{-3} M				Excess Morin, 1.32×10^{-4} M			
Trial	(Morin) M/1 x 10^6	pH	A_{413}*	Trial	(Pr^{+++}) M/1 x 10^6	pH	A_{413}**
1.	6.61	5.00	0.155	1.	2.84	5.00	0.038
2.	13.23	5.00	0.270	2.	5.68	5.00	0.116
3.	19.85	5.00	0.430	3.	7.10	5.00	0.182
4.	26.47	5.00	0.515	4.	8.52	5.00	0.244
5.	33.08	5.00	0.705	5.	11.35	5.00	0.382
6.	39.70	5.00	0.790	6.	14.19	5.00	0.539
7.	46.32	5.00	0.940	7.	17.03	5.00	0.588
8.	52.94	5.00	1.085	8.	19.87	5.00	0.780
				9.	21.29	5.00	0.852
				10.	22.71	5.00	0.878

*Absorbance corrected for excess Pr(III) contribution
**Absorbance corrected for excess morin contribution
From Figure 29, slope of line 1, 1.98×10^4; slope of line 2, 4.278×10^4.
The ratio of the slopes is 1.00/2.16.

Table A-IX. Slope Ratio Data for Neodymium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Excess Nd(III), 5.55 x 10^{-3}M (Morin) M/1 x 10^{6}	pH	A_{414}*	Trial	Excess Morin, 1.32 x 10^{-4} M (Nd^{+++}) M/1 x 10^{6}	pH	A_{414}**
1.	6.61	5.00	0.085	1.	2.77	5.00	0.198
2.	13.23	5.00	0.205	2.	5.55	5.00	0.265
3.	19.85	5.00	0.290	3.	6.93	5.00	0.347
4.	26.47	5.00	0.430	4.	11.09	5.00	0.495
5.	33.08	5.00	0.570	5.	13.87	5.00	0.638
6.	39.70	5.00	0.685	6.	16.64	5.00	0.816
7.	46.32	5.00	0.785	7.	19.41	5.00	0.868
8.	52.94	5.00	0.940	8.	20.80	5.00	0.899
				9.	22.19	5.00	1.041

*Absorbance corrected for excess Nd(III) contribution
**Absorbance corrected for excess morin contribution
From Figure 30, slope of line 1, 1.81 x 10^{4}; slope of line 2, 3.91 x 10^{4}.
The ratio of the slopes is 1.00/2.10.

Table A-X. Slope Ratio Data for Thulium (III)-Morin Complex in 50-50 DW at 25°C

Trial	Excess Tm(III), 4.74 x 10^{-4} M (Morin) M/1 x 10^{6}	pH	A_{423}*	Trial	Excess Morin, 1.32 x 10^{-4} M (Tm^{+++}) M/1 x 10^{6}	pH	A_{423}**
1.	6.61	5.00	0.125	1.	2.37	5.00	0.039
2.	13.23	5.00	0.250	2.	4.75	5.00	0.173
3.	19.85	5.00	0.340	3.	5.92	5.00	0.263
4.	26.47	5.00	0.530	4.	7.10	5.00	0.332
5.	33.08	5.00	0.620	5.	9.47	5.00	0.451
6.	39.70	5.00	0.765	6.	11.84	5.00	0.559
7.	46.32	5.00	0.880	7.	14.21	5.00	0.663
8.	52.94	5.00	1.050	8.	16.57	5.00	0.737
				9.	17.76	5.00	0.816
				10.	18.94	5.00	0.921

*Absorbance corrected for excess Tm(III) contribution
**Absorbance corrected for excess morin contribution
From Figure 31, slope of line 1, 1.98 x 10^{4}; slope of line 2, 4.46 x 10^{4}.
The ratio of the slopes is 1.00/2.25.

Table A-XI. Absorbance Change for Terbium (III) and Cerium (III)-Morin Complexes when Varying Lanthanide (III) concentration in presence of excess Morin in 50-50 DW at 25°C

Trial	Excess Morin, 1.32×10^{-4} M (Tb^{+++}) M/1 x 10^6	pH	A_{417}*	Trial	Excess Morin, 1.32×10^{-4} M (Ce^{+++}) M/1 x 10^6	pH	A_{413}*
1.	2.52	5.00	0.052	1.	2.85	5.00	0.043
2.	5.03	5.00	0.158	2.	5.71	5.00	0.171
3.	6.29	5.00	0.224	3.	7.14	5.00	0.243
4.	7.55	5.00	0.294	4.	8.56	5.00	0.304
5.	10.07	5.00	0.436	5.	11.42	5.00	0.432
6.	12.58	5.00	0.587	6.	14.27	5.00	0.555
7.	15.10	5.00	0.679	7.	17.13	5.00	0.668
8.	17.62	5.00	0.810	8.	19.98	5.00	0.786
9.	18.88	5.00	.856	9.	21.41	5.00	0.848
				10.	22.84	5.00	0.909

*Absorbances corrected for excess morin contribution.
Data plotted in Figure 32.