

Luminescence Study on Some Terbium(III) Complexes in Water and Water-Ethanol Mixtures

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The luminescence intensity of Tb³⁺ bound to picolinic acid, squaric acid, and 2,3-pyrazinedicarboxylic acid has been studied in water and water-ethanol mixtures. It has been found that the emission intensity of Tb³⁺ in the complexes is enhanced with the increase of ethanol content in water-ethanol mixtures. Several factors affecting on the emission intensity of Tb³⁺ in water-ethanol mixtures are discussed.

Introduction

Relatively less has been studied about luminescence of lanthanide ions in aqueous solution than their absorption properties. It is well known that luminescence intensity of lanthanide ions in solution depends strongly on the environment around the metal ion. The luminescence intensity is enhanced when the metal ion forms chelates with polydentate ligands¹⁻³. This emission enhancement by the complex formation in aqueous solution accounts for the shielding of the metal ion from water molecules being as a quencher and for the energy transfer from the ligand to the metal ion^{1,3}. On the other hand, each water molecule acting as a quencher takes place through a dynamic equilibrium between water molecules in the bulk and in the solution layer⁴. The quenching in hydrated lanthanide ions occurs via the coupling of excited *f* electron energy levels with that of OH vibration of water molecule⁵⁻⁸. The degree of quenching effect depends on the number of water molecules in the inner hydration sphere of the lanthanide ion^{8,9}.

A solvated metal ion in aqueous solution has the inner hydration sphere in which water molecules are directly interacting with the metal ion, and the outer hydration sphere in which the interaction between water molecules is influenced indirectly by the metal ion. When water soluble cosolvent such as ethanol is added, the hydration sphere around the metal ion would be changed. It has been recognized¹⁰ that the behavior of the thermodynamic, kinetic, spectral, and other physical properties of metal complexes in aqueous-ethanol binary solvents is varied with the variation of compositions of the mixtures. Those properties are closely related to the degree of structuredness at various compositions of the mixed solvents. Thus, it is expected that the effect of added organic solvent on the structure of water will likely be reflected in the luminescence intensity of the lanthanide ions of the chelates in aqueous-ethanol binary mixtures.

In this study, we have measured the emission intensities of Tb³⁺ bound to various chelating ligands at various compositions of aqueous-ethanol binary solvents to see the effect of

solvent structure on the complex formation.

Experimental

Excitation and emission spectra were recorded on Jovin Yvon Spectrofluorometer JY3 equipped with an 150 W Xe-arc lamp. Band widths were selected by using 4 or 10 nm slits. Absorption intensities were measured on Jovin Yvon Duospac 203. All pH measurements were made on a Tacussel PHN 78 pH meter with a combination electrode. The KCl solution of the electrode was replaced by saturated NaCl solution to prevent the precipitation of KClO₄ at electrode junction.

The stock solution of Tb³⁺ ion was prepared by dissolving Tb₄O₇ (99.999 %, Aldrich Chemical Co.) in a minimum amount of concentrated HClO₄ solution. The oxide of Tb⁴⁺ is reduced to Tb³⁺ evolving oxygen in solution. After evaporating excess acid, the solution was diluted with distilled water. The stock solution was standardized by EDTA titration under xylenol orange indicator and acetate buffer. The stock solution of Tb³⁺ was kept in pH ~3 to prevent the hydrolysis of the metal ion.

The ligand stock solutions of picolinic acid (ICI), squaric acid (Sigma Chem. Co.) and 2,3-pyrazinedicarboxylic acid (Aldrich Chem. Co.) were prepared by dissolving each acids in distilled water, respectively. The ligand stock solutions were standardized by the standard acid-base titration. Analytical grade ethanol (99.8 %, Merck Co) was used without further purification. The purity of the ethanol used was checked with the gas chromatography. NaClO₄ was used to adjust the total ionic strength of the working solution to 0.1 M. All luminescence measurements were carried out at a temperature of 20 ± 3°C.

Results and Discussion

The emission intensity of ⁵D₄→⁷F₆ transition of Tb³⁺ ion at ~491 nm was measured instead of that of ⁵D₄→⁷D₅ transition at ~545 nm to avoid the possible scattering interference from excitation wavelength around 272 nm.

The emission intensities of Tb³⁺ bound to various ligands are relative values to the emission intensity of 1 × 10⁻³ M per-

chlorate solution of Tb^{3+} . The emission spectra of Tb^{3+} bound to picolinate, squarate and 2,3-pyrazinedicarboxylate have shown the maximum excitation peaks at 268, 272 and 280 nm, respectively, while that of the perchlorate solution at 222nm. The ligand excited at corresponding wavelength does not produce its own emission spectrum whether the Tb^{3+} ion is present in the solution or not.

The relative emission intensities of Tb^{3+} bound to the ligands measured in water and water-ethanol mixtures are given in Table 1. pH dependence of Tb^{3+} emission of the

TABLE 1: Relative UV Absorption of Ligands and Relative Luminescence ($^5D_4 \rightarrow ^7F_6$ of Tb^{3+} , 491 nm) intensity of Tb^{3+} - Complexes in Water and in Water-Ethanol Mixtures

Ligand	Molar absorptivity of ligand	pH	Relative Luminescence Intensity		
			[L]/[M]	0.23mole fraction of ethanol	0.44mole fraction of ethanol
Picolinic acid	4.000 (265nm)	7.0	1.06	41	200
			2.13	90	410
			5.32	170	830
			10.64	240	950
Squaric acid	28,000 (265nm)	5.5	0.79	6	36
			1.05	7	45
			1.58	13	63
			1.05	3	13
2,3-Pyrazine-dicarboxylic acid	7,000 (276nm)	6.0	2.10	5	23
			5.26	8	41
			10.52	10	53

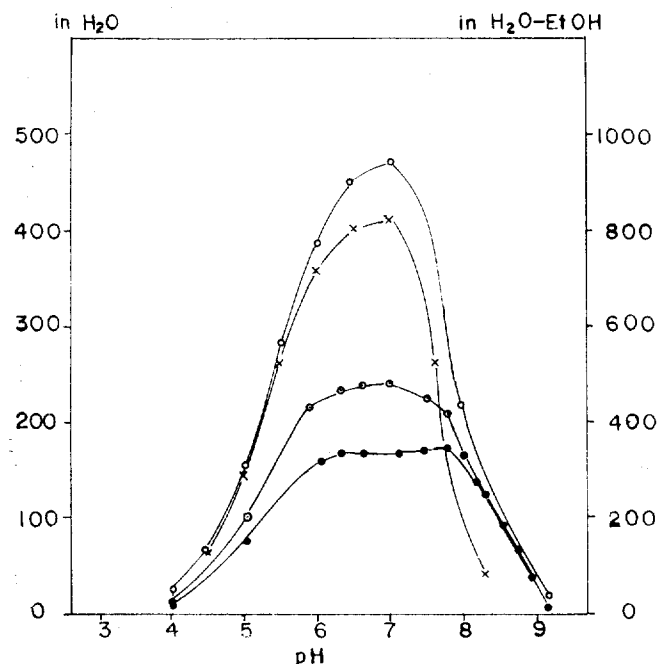


Figure 1. pH dependence of relative luminescence ($^5D_4 \rightarrow ^7F_6$ of Tb^{3+} , 491nm) intensity of Tb^{3+} -picolinate. —●—; [L]/[M]=5.32, in water. —×—; [L]/[M]=5.32 in 0.23 mole fraction of ethanol. —○—; [L]/[M] = 10.64 in water. —○—; [L]/[M]=10.64 in 0.23 mol fraction of ethanol. $\mu = 0.1$ M $NaClO_4$, $20 \pm 3^\circ C$.

complexes has been observed and the results are shown in Figures 1,2 and 3 for picolinate, squarate and 2,3-pyrazinedi-

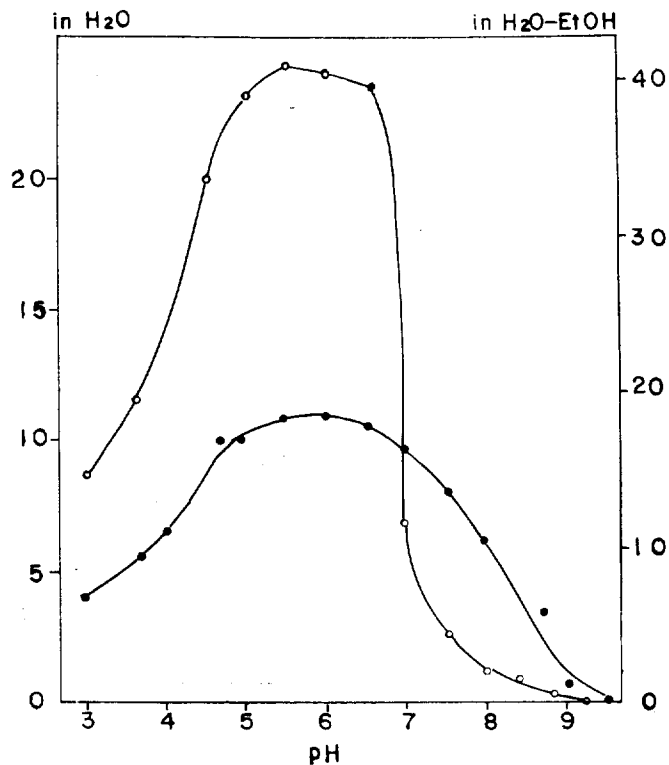


Figure 2. pH dependence of relative luminescence ($^5D_4 \rightarrow ^7F_6$ of Tb^{3+} , 491nm) intensity of Tb^{3+} -squarate. —●—; [L]/[M] = 1.05 in water. —○—; [L]/[M] = 1.58 in 0.23 mole fraction of ethanol. $\mu = 0.1$ M $NaClO_4$, $20 \pm 3^\circ C$.

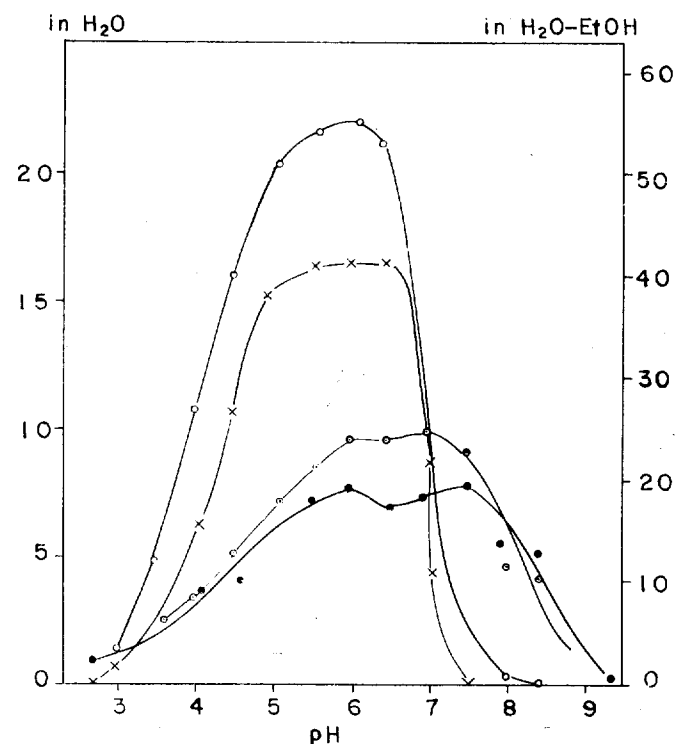


Figure 3. pH dependence of relative luminescence ($^5D_4 \rightarrow ^7F_6$ of Tb^{3+} , 491nm) intensity of Tb^{3+} -2,3-pyrazinedicarboxylate. —●—; [L]/[M]=5.26 in water. —○—; [L]/[M] = 5.26, in 0.23 mole fraction of ethanol. —×—; [L]/[M]=10.52 in water. —○—; [L]/[M] = 10.52 in 0.23 mole fraction of ethanol. $\mu = 0.1$ M $NaClO_4$, $20 \pm 3^\circ C$.

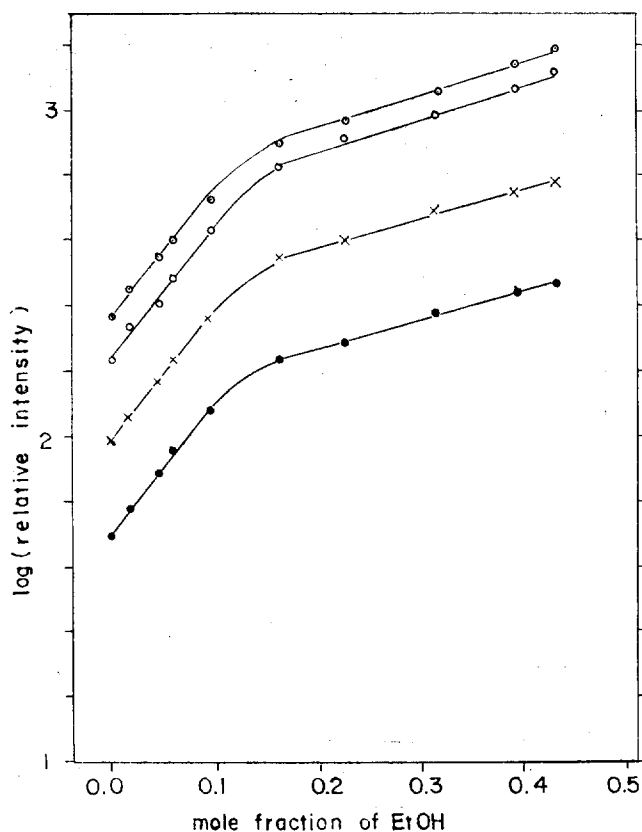


Figure 4. Relative luminescence (${}^5D_4 \rightarrow {}^7F_6$ of Tb^{3+} , 491nm) intensity of Tb^{3+} -picolinate as a function of mole fraction of ethanol in water-ethanol mixtures. —●—; $[L]/[M] = 1.06$. —×—; $[L]/[M] = 2.13$. —○—; $[L]/[M] = 5.32$. —⊙—; $[L]/[M] = 10.64$. pH = 7.0, $\mu = 0.1$ M $NaClO_4$, $20 \pm 3^\circ C$.

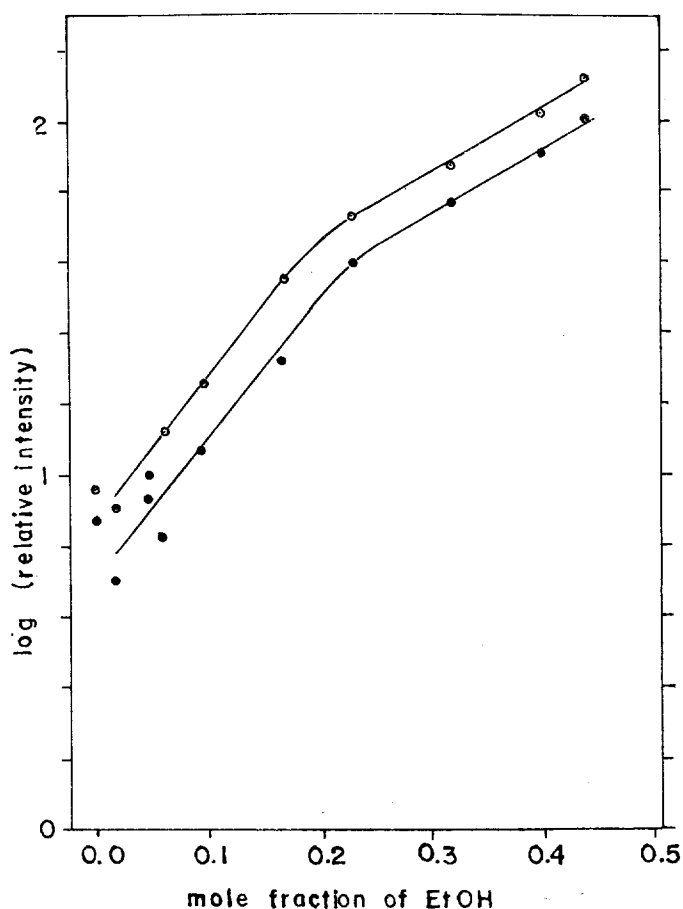


Figure 6. Relative luminescence (${}^5D_4 \rightarrow {}^7F_6$ of Tb^{3+} , 491nm) intensity of Tb^{3+} -2,3-pyrazinedicarboxylate as a function of mole fraction of ethanol in water-ethanol mixtures. —●—; $[L]/[M] = 5.26$. —⊙—; $[L]/[M] = 10.52$. pH = 6.0, $\mu = 0.1$ M $NaClO_4$, $20 \pm 3^\circ C$.

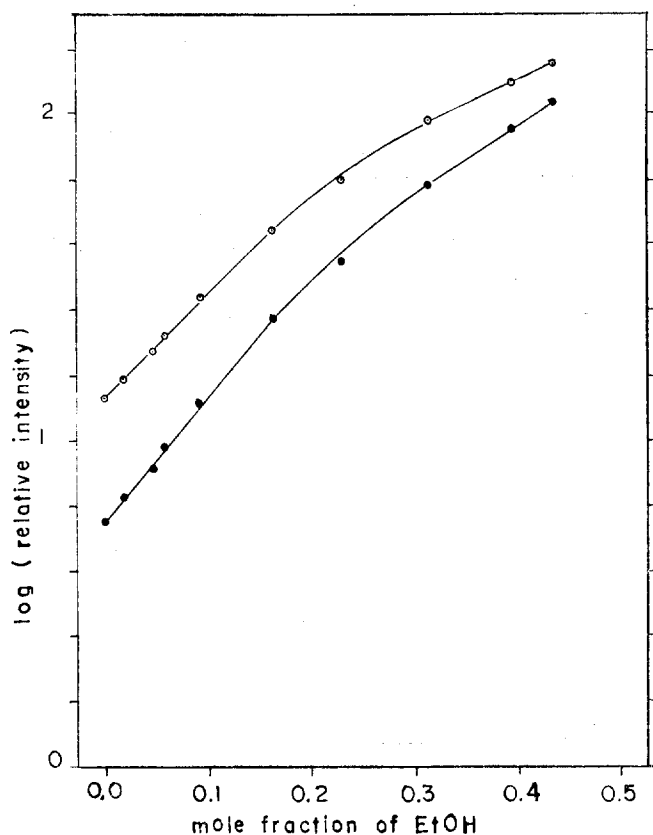


Figure 5. Relative luminescence (${}^5D_4 \rightarrow {}^7F_6$ of Tb^{3+} , 491nm) intensity of Tb^{3+} -squarate as a function of mole fraction of ethanol in water-ethanol mixtures. ●; $[L]/[M] = 0.79$. ⊙; $[L]/[M] = 1.58$. pH = 5.5, $\mu = 0.1$ M $NaClO_4$, $20 \pm 3^\circ C$.

carboxylate ligands, respectively. The maximum emission intensity is observed at a pH of 7.0 for picolinate complex and at a pH of 5.5 for squarate complex both in water and water-ethanol mixture. For 2,3-pyrazinedicarboxylate the maximum point is appeared at slightly lower pH in water-ethanol mixture than in water solvent, thus a pH of 6.0 was chosen as the hydrogen ion concentration fulfilling the condition of maximum intensity both in water and water-ethanol mixtures.

The emission intensity of Tb^{3+} in picolinate, squarate, and 2,3-pyrazinedicarboxylate complexes as a function of the mole fraction of ethanol in water-ethanol mixtures has been measured at the pH shown the maximum emission enhancement. Figures 4 through 6 show the relationship of the intensity in logarithm as a function of mole fraction of ethanol in the solvent.

It has been reported³ that efficient ligands promoting Tb^{3+} emission are those having a capability of forming chelate rings among benzenecarboxylic acid derivatives. All ligands studied have the aromaticity and the ability to form chelate rings. Table 1 shows that picolinate is the most efficient in promoting Tb^{3+} emission. Even though squarate has about seven times higher molar absorptivity than picolinate, the later ligand enhances the Tb^{3+} emission much higher. This would mean that the complexing ability of picolinate is much better than that of squarate. The stability constant of

terbium picolinate in aqueous solution is about 10 times greater than that of terbium squarate. The $\log \beta_1$ of Tb^{3+} -picolinate¹¹ is 3.79 and that of Tb^{3+} -squarate¹² is 2.87. It has been suggested² that the important factor in the transfer of energy from *o*-benzoylbenzoate to Eu^{3+} in ethanol-water mixtures is the formation of a complex between the ligand donor and the metal ion acceptor, and the intensity of emission is proportional to the concentration of the complex. The lower luminescence intensity enhancement of Tb^{3+} of 2,3-pyrazinedicarboxylate would be due to the lower stability of the complex expected. The 2,3-pyrazinedicarboxylate would form seven membered chelate ring with terbium ion through the two oxygen atoms of two carboxylate groups in the ligand. However, higher stability of the complex could not be expected because of its undesirable large ring size and the electron withdrawing effect of the pyrazine ring of the ligand. The thermodynamic study on the formation of lanthanide 2,3-pyrazinedicarboxylate complexes is presently undertaken in this laboratory.

As seen from Figures 4,5 and 6, the \log of emission intensity of Tb^{3+} increases linearly with the increasing of the mole fraction of ethanol in water-ethanol mixtures with an inflection point around 0.20 mole fraction of ethanol. Interestingly the slope of the linear line is constant regardless of the ligand to metal ratio in the given system. There might be several factors affecting on the emission intensity of Tb^{3+} in this mixed solvent. The addition of ethanol to water gives the alteration of physicochemical properties of the solvent, such as the dielectric constant¹³, the hydrogen bonding or the bulky structure of water¹⁰. Firstly, decreasing of the dielectric constant of the mixed solvent as increasing of ethanol content may induce the stronger ionic interaction between Tb^{3+} ion and the ligand, thus the higher stability of the complex. Such strengthened bond of the complex make not only the energy transfer from the ligand to Tb^{3+} ion be more efficient, but also reduce the number of hydrated water molecules acting as the quencher in the inner sphere of the metal ion. Secondly, the presence of a small quantity of ethanol which is less polar than water would enhance the hydrogen bonding of water¹⁰. This effect of the structure making may weaken the interaction

of Tb^{3+} with water molecules in the inner hydration sphere. Therefore, it would be expected that the emission intensity of Tb^{3+} increases as whole as the ethanol content increases in water-ethanol mixtures.

However, above about 0.20 mole fraction of ethanol in water-ethanol mixtures, the hydrogen bonding of the solvent may be partly broken by the addition of ethanol. This structure breaking effect of added ethanol may strengthen the hydration of Tb^{3+} ion. Thus the excited state of Tb^{3+} would be more effectively quenched by the water molecules. Since this increased quenching effect above about 0.20 mole fraction of ethanol could reduce the degree of increasing the emission intensity, an inflection point would be appeared on the line of the intensity against the mole fraction of ethanol in water-ethanol mixtures.

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