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Characteristics of Coordination Compounds of Calcein Blue for a Tunable Organic Liquid Laser

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The lasing and spectroscopic properties of coordination compounds of Calcein Blue with aluminium, calcium, strontium, and barium in water and in a water-ethanol mixture were investigated. The chelate formation improved the lasing properties of Calcein Blue, since the fluorescence quantum yield was increased by the formation of rigid rings in the molecule, and the lasing wavelength could be modified by the metal ion. By using these coordination compounds, tunable laser emissions were observed in the spectral range of 400—478 nm with a low threshold excitation intensity. The threshold excitation intensities excited by the nitrogen laser, the pulse width of which was very short (2.5 ns), were formulated by means of the spectral parameters for such molecules as its Stokes shift was large and its singlet-singlet absorption could be ignored. The calculated values obtained by this formula agreed well with the experimental values in water.

The organic liquid laser has proved itself to be an effective tool for the spectroscopy of atoms and molecules because of its intense power, its narrow bandwidth, and the tunability of its wavelength. Up to this time the organic dyes and scintillators, the fluorescence quantum efficiencies of which are high, have been used as laser materials. The properties of dyes have been improved to obtain a high conversion efficiency, a wide tuning range, a high solubility especially in water, and a high stability. The rigid ring formation of an amide group of coumarin reduces the energy transfer to the vibrational and rotational states and improves the quantum efficiency of the dye.¹⁾ The tuning range is expanded by broadening the fluorescence spectrum in the presence of acidic exciplexes and a neutral form of 4-methylumbelliferone.²,³⁾ The gain of the organic liquid laser is, however, generally small probably because of its wide fluorescence spectrum. The surfactant increases the solubility of the laser material in water and reduces the thermal fluctuation of the refractive index of the dye solution in the case of a continuous oscillation of the dye laser.¹⁾ The chemical stability of dyes is increased by the trifluoromethylation of the methyl group of 7-diethylamino-4-methylumbelliferone.⁴⁾ Nevertheless, there is a need for a laser material with a higher conversion efficiency, a wider tuning range, a higher solubility in water, and a higher chemical stability, especially in the ultraviolet region.

The gain spectroscopy and the threshold analysis provide useful information on the lasing property and the improvement of the laser material. The gain spectroscopy of 4-methylumbelliferone³⁾ and the threshold analysis of rhodamine B and 6G⁵,⁶⁾ have been carried out previously. However, the threshold analysis under a short-pulse excitation has not been carried out in detail.

The laser action of the coordination compound with a sufficiently high quantum efficiency is expected if there is no particular quenching by the metal ion. Two kinds of organic chelate lasers have hitherto been reported. One of them is europium benzoylacetonate,⁷⁾ the first organic laser: its laser emission is due to the emission from a metal ion and its spectral range is very narrow. The other one is the metal phthalocyanine,⁸,⁹⁾ the first organic liquid laser: its spectral property can not be modified reversibly, for example by varying the pH of the solution, and it behaves as an organic dye, as it is usually called.

The laser action of Calcein Blue(4-methylumbelliferone-methyleneiminodiacetic acid) has been reported previously, and the effect of oxygen in the solution has been investigated.¹⁰⁾ On the other hand, Calcein Blue is well-known as a metalfluorechromic indicator in the complexometric determination of zirconium,¹¹⁾ gallium,¹²⁾ and some alkali earth metals.¹³⁾

In the previous letter, we have reported that the coordination compounds of Calcein Blue with aluminium, calcium, strontium, and barium can give laser emission and that the spectral properties of the coordination compound can be modified by changing the metal ions or by varying the pH of the solution.¹⁴⁾ In the present study, a further investigation of the spectral properties and laser characteristics of the coordination compounds of Calcein Blue and the threshold analysis of these lasers has been carried out for the purpose of finding excellent laser materials.

Experimental

Apparatus (Lasers). An experimental arrangement to obtain laser emission is shown in Fig. 1. The exciting source used is a nitrogen laser, which is similar to that described by Basting *et al*,¹⁵⁾ and by Maeda and Miyazoe.¹⁶⁾ It has a 30 cm tube and two 8 nF capacitors made of polyester films and aluminium foils. The output power is 700 kW at 20 kV input, and the pulse width is 2.5 ns (measured by

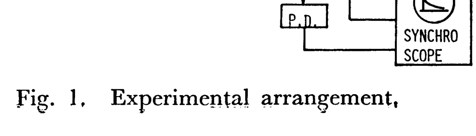


Fig. 1. Experimental arrangement.

a Tektronix 519 oscilloscope). The intense peak power and the short pulse width of the nitrogen laser are suitable for the excitation of an organic liquid laser and for the threshold analysis.

The ultraviolet output of a pulsed nitrogen laser is focused by a spherical lens L_1(f=10 cm) on the surface of the solution of the laser material in a square quartz cell (1×1×5 cm). The cavity of the liquid laser consists of two dielectric coated mirrors with reflectivities of 100 percent (M_1) and 95 percent (M_2), respectively. In the case of tuning the laser oscillation the mirror with 100 percent reflectivity was replaced by a grating (Hitachi Ltd. 3×3 cm, 500 nm blaze, 600 groove/mm) and the square quartz cell was replaced by a quartz cell with nonparallel sides. The laser oscillation of the coordination compound was detected by means of a photocell and was confirmed by observing the coherent radiation. The spectra of the laser emission were photographed by means of an Adam Hilger prism monochromator, and the wavelength was calibrated by a low-pressure mercury lamp. A part of nitrogen laser emission was taken out by a quartz plate (P_1) and was detected by a photodiode (NEC LSD 39A; bandwidth 1 GHz). The signal was integrated by a capacitor (C=3000 pF, R=200 kΩ, and the peak intensity was measured by means of a synchroscope (Iwatsu SS5157).

Apparatus (Fluorescence and Absorption Spectra). The fluorescence spectrum was measured by means of a Hitachi MPF 4 fluorescence spectrophotometer; its spectral response was calibrated by using a rhodamine B cell. The fluorescence spectrum of a concentrated solution was measured in the similar configuration of a quantum counter system using a triangle cell, in which the incident light irradiated the hypotenuse surface of the sample and the fluorescence was measured at a right angle to the incident radiation. The dependence of the fluorescence intensity (peak value) on the concentration of 4-methylumbelliferone was measured by this method. The fluorescence intensity is independent of its concentration above 10^{-4} mol/l. This shows that the excitation light is absorbed completely and that the emission intensity is dependent only on its quantum efficiency, not on its absorbance. The true emission spectrum normalized by the quantum efficiency and the quantum efficiency of the concentrated solution can be measured directly without diluting the solution. It is necessary to use a concentrated solution, since the properties in the concentrated solution may differ from those in the dilute solution because of the difference in the degree of aggregation which may occur in high concentrations. Some deviation from the true fluorescence spectrum due to the self-absorption may occur; however, it is small for 4-methylumbelliferone, Calcein Blue, and its complexes, since the superposition of the fluorescence and absorption spectra is very small (below 1 percent).

The absorption spectra were measured in a split-beam method by using a Hitachi 356 two wavelength/double-beam spectrophotometer.

Reagents. The 4-methylumbelliferone (Tokyo Kasei) was recrystallized twice from water and ethanol to obtain transparent crystals. The Calcein Blue (Dojindo Lab.) was used without purification. The calcium chloride (guaranteed grade; Kishida Chemical Co.), strontium chloride (guaranteed grade; Kishida Chemical Co.), barium chloride (guaranteed grade; Ishizu Pharmaceutical Co.), and aluminium ammonium sulfate (guaranteed grade; Wako Pure Chemical Ind.) were used without purification.

Procedure. A 2.5×10^{-3} mol/l solution of Calcein Blue was prepared by dissolving 0.0803 gram of Calcein Blue and by diluting the solution to 100 ml with freshly distilled water, and adjusted to below pH 4 by adding a buffer solution of sodium acetate. A 10^{-3} mol/l sample solution was prepared by adding the following solutions to a 25 ml volumetric flask in turn; 10 ml of 2.5×10^{-3} mol/l Calcein Blue, a few ml of a 2.5×10^{-3} mol/l metal ion solution (10 ml was used for the formation of the 1 : 1 complex), a solution of sodium acetate, ammonia, or sodium hydroxide to adjust the pH from 4 to 13, and distilled water. The coagulation of aluminium ions or the precipitation of calcium, strontium, and barium hydroxides and carbonates, which disturb the laser action by the scattering of the laser beam, can be reduced by this procedure.

Results

Spectral Properties of Calcein Blue. Calcein Blue has a methyleneiminodiacetic acid group on the 8 position of 4-methylumbelliferone and exhibits three forms(denoted by (1), (2), and (3)) at the respective pH regions, as is shown in Fig. 2. The UV absorption

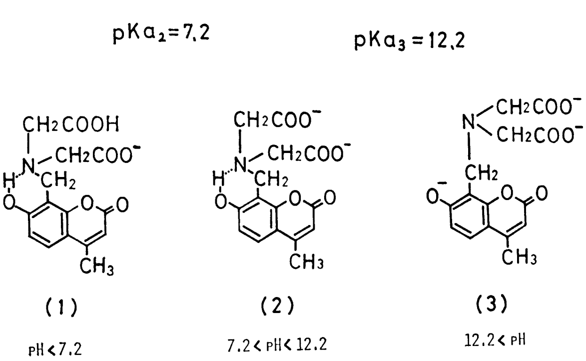


Fig. 2. Structure of Calcein Blue.
The form (1) has two ionizable hydrogen atoms (below pH 7.2). The form (2) has one ionizable hydrogen atom (pH 7.2—12.2). The form (3) has no ionizable hydrogen atom (above pH 12.2).

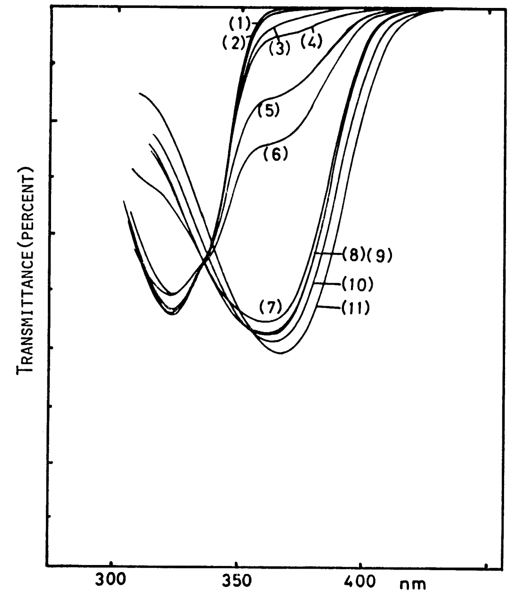


Fig. 3. Absorption spectra of Calcein Blue at various pH.
pH: (1) 3.3 (2) 4.4 (3) 5.1 (4) 6.0 (5) 6.6 (6) 6.8 (7) 8.6 (8) 9.6 (9) 10.2 (10) 11.7 (11) 12.8 concentration: 2.5×10^{-5} mol/l.

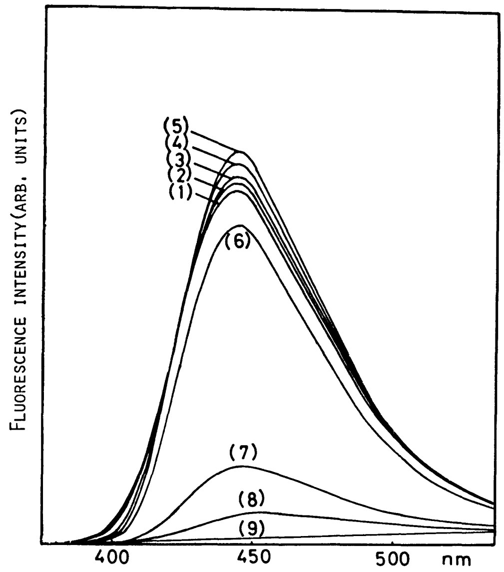
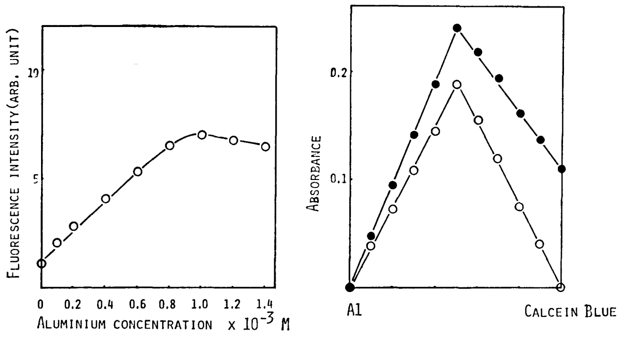


Fig. 4. Fluorescence spectra of Calcein Blue at various pH.
pH: (1) 3.3 (2) 4.2 (3) 5.1 (4) 7.6 (5) 9.5 (6) 11.5 (7) 12.7 (8) 13.4 (9) blank. Concentration: 10^{-3} mol/l, $\lambda_{ex}=337$ nm.



(1) (2)

Fig. 5. Composition of aluminium Calcein Blue.
(1) Mole ratio plot of the fluorescence intensity. Concentration of Calcein Blue: 10^{-3} mol/l, $\lambda_{ex}=337$ nm, $\lambda_{em}=410$ nm, pH=5.0.
(2) Continuous variation plot of absorbance. (●): Experimental values, (○): the absorbance of the coordination compound, which is obtained by substructing the absorption of Calcein Blue from the experimental value, concentration of the mixture: 4.0×10^{-4} mol/l, pH=5.0, $\lambda_{abs}=350$ nm.

and fluorescence spectra were measured at various pH values and are shown in Figs. 3 and 4. The existence of three forms of Calcein Blue is confirmed since two isosbestic points are observed at 335 and 354 nm in the UV spectra. As the form of Calcein Blue changes from (1) to (2), the maximum of the absorption band shifts to longer wavelengths: however, the extinction coefficient at 337 nm (the lasing wavelength of the nitrogen laser) does not vary. The wavelength of the maximum emission does not move, and the intensity increases gradually. The small variation in the fluorescence quantum efficiency may be due to the small deformation in the structure by the dissociation of the hydrogen ion (Fig. 2 (1), (2)). As the form changes from (2) to (3), the extinction coefficient at 337 nm gradually decreases, while the fluorescence intensity decreases steeply. Calcein Blue in the form (3) is non-fluorescent, since the side chain, the methyleneiminodiacetic acid group, becomes flexible by the breakage of the hydrogen bond.[17]

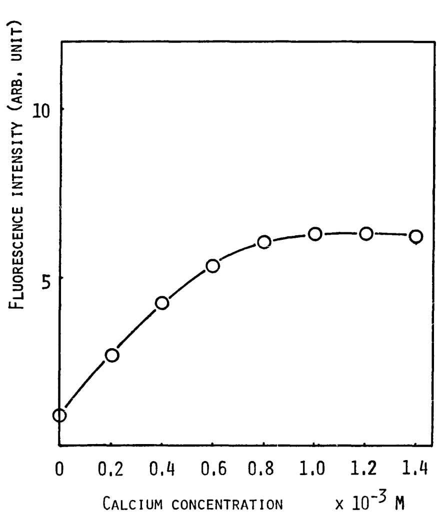


Fig. 6. Composition of calcium Calcein Blue.
Mole ratio plot of the fluorescence intensity. Concentration of Calcein Blue: 10^{-3} mol/l, $\lambda_{ex}=337$ nm, $\lambda_{em}=450$ nm.

The dependences of the molar extinction coefficient of Calcein Blue at 370 nm and that of the fluorescence intensity at 446 nm on the pH were measured; the acid dissociation constants of pK_a2 and pK_a3 were determined to be about 7.2 and 12.2 respectively.

Composition of Coordination Compound. The color change in the solution of Calcein Blue from blue to violet upon the addition of aluminium ions implies the formation of a coordination compound. The dependence of the fluorescence intensity of the aluminium Calcein Blue on the aluminium concentration was measured in order to determine the composition of the complex; the mole ratio plot is shown in Fig. 5 (1). The figure indicates that a 1 : 1 binary complex of aluminium Calcein Blue is formed at pH 5, since the fluorescence intensity increases as the concentration of the aluminium increases up to an equimolar composition. The gradual decrease in the aluminium excess region may be due to the light scattering by aluminium hydroxide formed in the solution. The absorbance of aluminium Calcein Blue was also measured; the continuous variation plot is shown in Fig. 5 (2). The maximum absorbance was obtained at the equimolar concentration, and the formation of a 1 : 1 binary complex was confirmed.

The dependence of the fluorescence intensity of calcium Calcein Blue on the calcium concentration is shown in Fig. 6. The fluorescence intensity is constant above the equimolar concentration. Accordingly, the metal ion was mixed in a 1 : 1 proportion to the ligand molecule for the preparation of the coordination compound.

Spectral Properties of Aluminium Calcein Blue. The

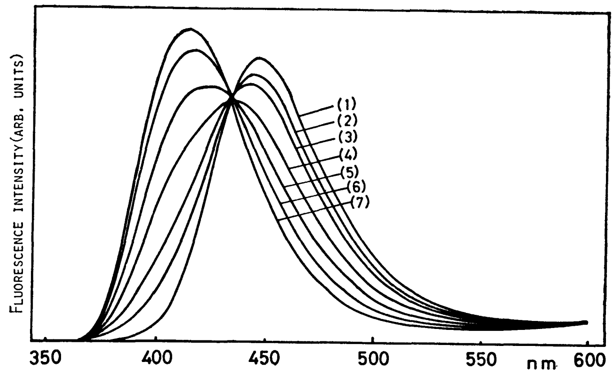


Fig. 7. Fluorescence spectra of aluminium Calcein Blue at various aluminium concentration at pH 6.0. Concentration of Calcein Blue: 10^{-3} mol/l, $\lambda_{ex}=$ 337 nm, concentration of aluminium (mol/l): (1) 0 (2) 0.1×10^{-3} (3) 0.2×10^{-3} (4) 0.4×10^{-3} (5) 0.6×10^{-3} (6) 0.8×10^{-3} (7) 1.0×10^{-3}.

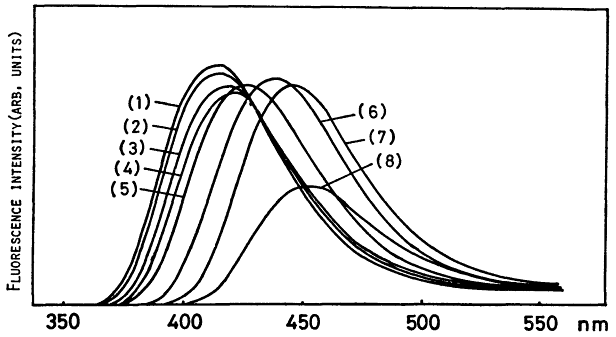


Fig. 8. Fluorescence spectra of aluminium Calcein Blue at various pH. Concentration of aluminium Calcein Blue: 10^{-3} mol/l, pH: (1) 5.0 (2) 6.0 (3) 7.1 (4) 7.9 (5) 9.0 (6) 10.0 (7) 11.0 (8) 12.0, $\lambda_{ex}=$ 337 nm.

fluorescence spectra of the coordination compound of aluminium Calcein Blue at various aluminium concentrations are shown in Fig. 7. The contribution of the coordination compound in the fluorescence spectrum increases as the aluminium concentration increases, as is indicated by the shift of the band to shorter wavelengths. The emission intensity of the coordination compound is stronger than that of the ligand molecule. The iso-emissive point shows that no side reaction takes place.

The effect of the pH on the fluorescence spectrum and the molar extinction coefficient at 370 nm of aluminium Calcein Blue (1 : 1 mixture) are shown in Figs. 8 and 9. The fluorescence spectrum shifts to longer wavelengths as the pH increases, since the complex dissociates to an ion and a ligand in this pH region. The coordination compound of aluminium Calcein Blue is formed predominantly below pH 5, and the equilibrium shifts to the dissociation and the release of a proton occur simultaneously, since the fluorescence spectra show no iso-emissive point.

It is well known that the quantum efficiency of the dyes and the complexes increases in a hydrophobic solvent since the interaction between the solute and the solvent decreases. The laser action is expected to be obtained in a ethanol–water mixture under a low excitation intensity. The dependences of the molar extinction coefficient and the fluorescence intensity of aluminium Calcein Blue on the volume percentage of ethanol in water were measured; they are shown in Fig. 10. Although the absorption and the fluorescence spectra do not shift, the extinction coefficient and the fluorescence intensity increase gradually as the ethanol volume percent increases. The quantum efficiency of the aluminium complex does not increase much, since it is already high and near unity in water. The small variation in the spectra indicates that the form and the composition of the coordination compound in

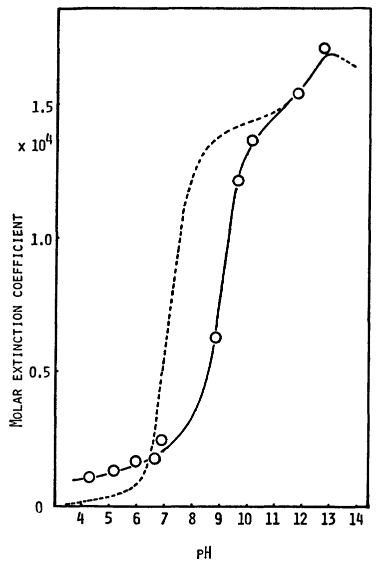


Fig. 9. Molar extinction coefficient at 370 nm at various pH. Solid curve: aluminium Calcein Blue, broken curve: Calcein Blue.

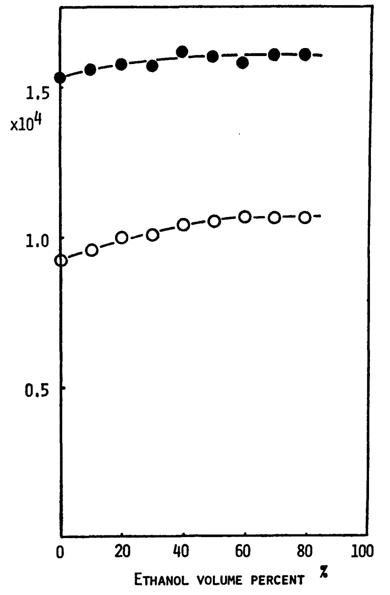


Fig. 10. Fluorescence intensity (○: arbitrary units) and molar extinction coefficient (●) of aluminium Calcein Blue in water–ethanol mixture. $\lambda_{ex}=337$ nm, $\lambda_{em}=446$ nm, $\lambda_{abs}=337$ nm.

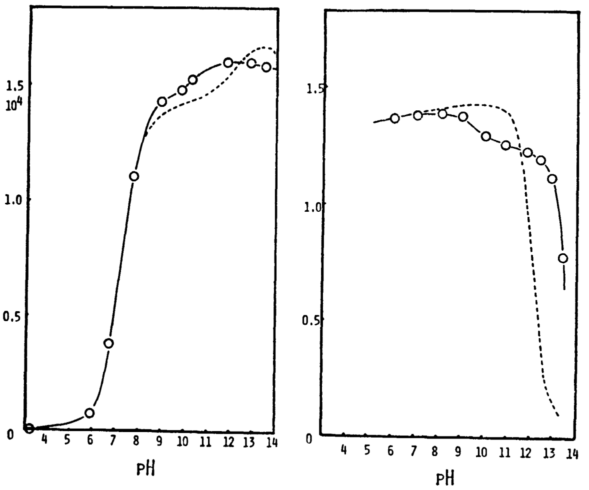


Fig. 11. Molar extinction coefficient (left) and fluorescence intensity (right: arbitrary units) at various pH. Solid curve: barium Calcein Blue, broken curve: Calcein Blue, $\lambda_{abs}=337$ nm, $\lambda_{ex}=337$ n,, $\lambda_{em}=$ 446 nm.

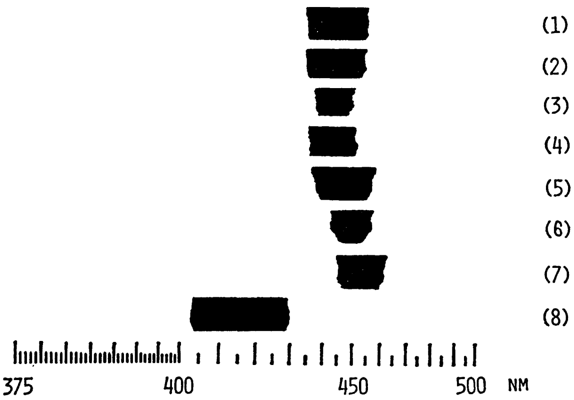


Fig. 12. Laser spectra of Calcein Blue and the complexes.
(1) Calcein Blue (pH 5) (2) Ca Calcein Blue (pH 5) (3) Sr Calcein Blue (pH 5) (4) Ba Calcein Blue (pH 5) (5) Ca Calcein Blue (pH 12) (6) Sr Calcein Blue (pH 12) (7) Ba Calcein Blue (pH 12) (8) Al Calcein Blue (pH 5).

an ethanol-water mixture are identical to those in water.

Spectral Properties of Barium and Calcium Calcein Blue. Barium and calcium Calcein Blue have intense fluorescences at about pH 9 and 13.[13)] The dependences of the molar extinction coefficient at 370 nm and the fluorescence intensity at 446 nm of barium Calcein Blue on the pH were measured in detail (*cf.* Fig. 11), in order to clarify the variation in the composition of the coordination compound. The coordination compound of barium Calcein Blue is formed in the region above pH 8, and it has an intense fluorescence even at pH 13. The structure of barium Calcein Blue in the pH 8—13.5 region is proposed to be the form in which a phenolic hydrogen is substituted by an alkali earth metal ion and the free side chain is bound by the metal ion.[13)] In this structure the barium ion may not be surrounded by the other oxygen atom, since the barium ion is doubly charged and the quantum yield is not so high as that of aluminium Calcein Blue.

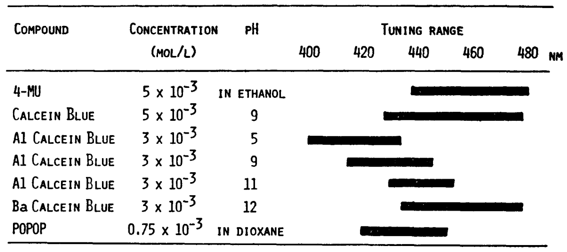


Fig. 13. Tuning ranges of lasers of dyes and coordination compounds.

Lasing Wavelength. The laser spectra of Calcein Blue and the coordination compounds are shown in Fig. 12. The laser action of Calcein Blue is observed at around 446 nm at pH 5, but not at pH 12. The coordination compounds of Calcein Blue with calcium, strontium, and barium lase at around 450, 452, and 454 nm respectively at pH 12. It is noteworthy that the coordination compound with an alkali earth metal ion lases at longer wavelengths as the atomic weight of the metal ion increases. The stability constant and the electrostatic force by the metal ion decrease as the atomic weight and the ion radius increase, and the perturbation of the calcium ion to the ligand molecule is expected to be stronger than that of barium. The red shift in the heavier atom complex might be due to the steric effect.

Calcein Blue forms a coordination compound with an aluminium ion at around pH 5, and it lases at around 418 nm; the wavelength is shorter than that of Calcein Blue.

Tuning Range. The tuning ranges (the wavelength ranges in which the narrow-band oscillation is possible) of the coordination compound lasers are shown in Fig. 13, where 4-methylumbelliferone and 1,4-bis(5-phenyloxazol-2-yl)benzene(POPOP) are included for the sake of comparison. Tunable laser emission from 436 nm to 480 nm was observed from the solution of Calcein Blue (pH 9). The tuning range of the aluminium Calcein Blue complex is 400—435 nm at pH 5 and it is longer in the wavelength at a higher pH value. The barium complex lases in the range of 435—478 nm, as in the case of 4-methylumbelliferone. In this way the laser action of the coordination compound of Calcein Blue can be observed in the range from near ultraviolet (400 nm) to blue green (478 nm) with a low threshold excitation intensity by changing the metal ion and by varying the pH. The full width at the half maximum of the laser emission was a few nanometer, which would be due to the short pulse width of the nitrogen laser (2.5 ns) and to the lack of the resolution of the grating. The dioxane solution of the POPOP shows superradiation (amplified spontaneous emission) in a solution more concentrated than 10^{-3} mol/l, and the tunable laser action was not observed at 10^{-3} mol/l.

Discussion

Threshold Analysis. The threshold equation of the laser action represents a relation between all the parameters affecting lasing; critical inversion, emission wavelength, losses, dye concentration, and extinction coefficient. The gain, α, of the organic liquid laser is written as[3]:

$$\alpha = \sum_i [\sigma_{\mathrm{em}i} N_i^* - \sigma_{\mathrm{s}i} N_i - k_i] - d \tag{1}$$

The summation in the equation shows the sum on such different species as the ligand and the coordination compound. In this equation, $\sigma_{\mathrm{em}i}$ is the emission cross section; $\sigma_{\mathrm{s}i}$, the singlet-singlet absorption cross section at the wavelength of the laser emission, and N_i and N_i^* the population in the ground and the excited states. The first term of this equation is the amplifying term due to the fluorescence; the second term is the loss term due to the singlet-singlet absorption at the lasing wavelength, and the third term, k_i, is the loss term due to the triplet-triplet absorption. The last term, d, represents the loss of the resonating cavity. The third term can be neglected because the pulse width of the excitation source of the nitrogen laser is short (2.5 ns) enough to be able to ignore the absorption from the triplet state.

The gain, α, can be set at zero under the threshold condition, thus,

$$\sum_i [\sigma_{\mathrm{em}i} N_i^* - \sigma_{\mathrm{s}i} N_i] - d = 0. \tag{2}$$

When there are only two species, such as a ligand and a complex, the weight-averages ($\bar{\sigma}_{\mathrm{em}}$ and $\bar{\sigma}_{\mathrm{s}}$) are substituted;

$$\bar{\sigma}_{\mathrm{em}} N^* - \bar{\sigma}_{\mathrm{s}} N - d = 0. \tag{3}$$

Then, the critical inversion, N^*/N, at the threshold is written as follows;

$$\left[\frac{N^*}{N}\right]_{\mathrm{threshold}} = \frac{\bar{\sigma}_{\mathrm{s}} + d/N}{\bar{\sigma}_{\mathrm{em}}}. \tag{4}$$

The rate of the formation of N^* by the excitation is represented by:

$$\frac{dN^*}{\mathrm{d}t} = \bar{\sigma}' I(t) N - \left(\frac{1}{\tau}\right) N^* \tag{5}$$

where $I(t)$ is the intensity of the excitation source; $\bar{\sigma}'$, the absorption cross section at the wavelength of the nitrogen laser, and τ, the lifetime of fluorescence. This differential equation gives the critical inversion, N^*/N, approximately as follows:

$$\frac{N^*}{N} \simeq \tau \bar{\sigma}' I(t). \tag{6}$$

From Eqs. 4 and 6, we obtain:

$$I_{\mathrm{threshold}} \simeq \frac{\bar{\sigma}_{\mathrm{s}} + d/N}{\tau \bar{\sigma}' \bar{\sigma}_{\mathrm{em}}}. \tag{7}$$

The absorption cross section, $\bar{\sigma}_{\mathrm{s}}$, at the lasing wavelength is small in the case of a coumarin compound, such as Calcein Blue and its complexes, because the Stokes shifts of these compounds are large and the superposition of the fluorescence and absorption spectra is rather small, and thus $\bar{\sigma}_{\mathrm{s}}$ can be neglected. When $\bar{\sigma}_{\mathrm{em}}$ $(=\lambda^4 E/8\pi c\eta^2\tau)$ is substituted,[3] Eq. 7 becomes:

$$I_{\mathrm{threshold}} \simeq \frac{8\pi c\eta^2 d}{N\bar{\sigma}'\lambda^4 E} \propto \frac{\eta^2 d}{n\bar{\varepsilon}\lambda^4 E}. \tag{8}$$

In this equation, E is the fluorescence intensity normalized by its quantum efficiency; η the refractive index; $\bar{\varepsilon}$, the weight-average of the molar extinction coefficient at the wavelength of the nitrogen laser, and λ the wavelength of the maximum fluorescence intensity. The observed value of the extinction coefficient can be used for $\bar{\varepsilon}$ in the equation. The population in the ground state can be set at the total concentration, n.[18]

The equation can clarify the characteristics of a laser material with a large Stokes shift. The threshold excitation intensity of a given compound can be calculated, and the usefulness of that compound as a laser material can be estimated by the use of spectral parameters. This threshold excitation equation shows the λ^4 term in the denominator requires a higher excitation intensity in the shorter wavelength region; thus, the laser material should be more efficient in this region.

Experimental Evidence for Eq. 8. The dependence of the threshold excitation intensity of the laser emission of 4-methylumbelliferone on the concentration was measured, as it is a typical coumarin compound. The linear relation of n *vs.* $1/I$ was obtained; it proves that the main loss is not the absorption of the laser material, but the loss in the laser cavity. Eq. 8 is thus confirmed.

Laser Emission of Calcein Blue. The threshold excitation intensity of Calcein Blue was calculated from the data of the absorption (Fig. 3) and fluorescence (Fig. 4) spectra; it is represented by the broken line in Fig. 14. The experimental results are also plotted in this figure. The threshold excitation intensity gradually decreases up to pH 11 as the percentage of the form (2) increases. Calcein Blue is non-fluorescent and does not lase above pH 12. The experimental values of the threshold excitation intensity agree well with the calculated ones; Eq. 8 is thus proved to be useful. The wavelength of the laser emission of Calcein Blue is 446 nm and is independent of the pH as in the case of the fluorescence spectrum.

Laser Emission of Aluminium Calcein Blue. The

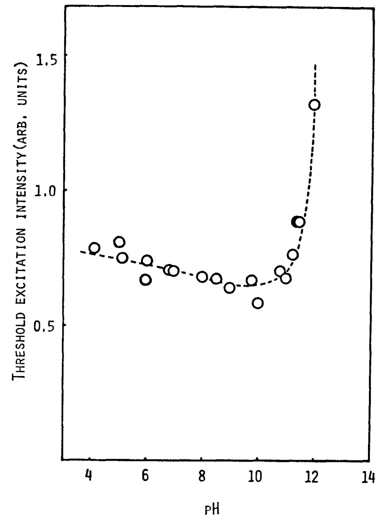
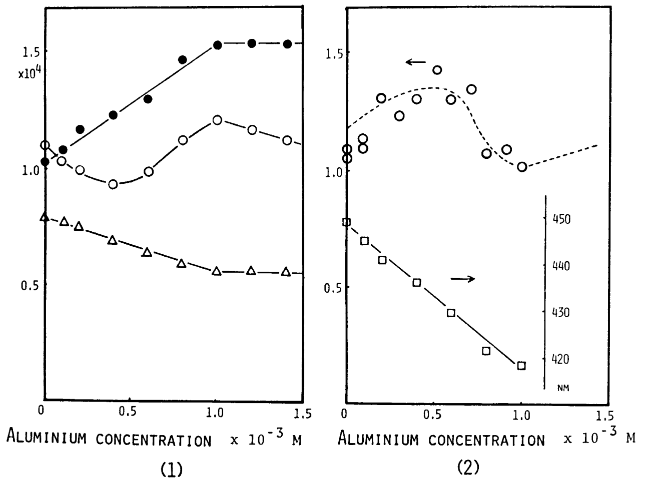
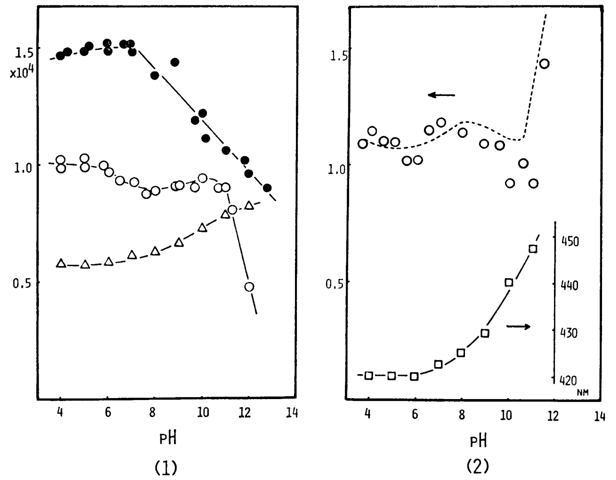


Fig. 14. Dependence of the threshold excitation intensity of Calcein Blue (arbitrary units, ----: calculated value, ○: experimental values) on pH.



(1) (2)

Fig. 15. (1) Dependences of the molar extinction coefficient $\bar{\varepsilon}$(●), the fluorescence intensity E(○: arbitrary units), and λ^4 (△: arbitrary units) of aluminium Calcein Blue on the aluminium concentration. (2) Dependences of the threshold excitation intensity (arbitrary units, ---: calculated value, ○: experimental values) and lasing wavelength (□) of aluminium Calcein Blue on the aluminium concentration. Concentration of Calcein Blue: 10^{-3} mol/l.



(1) (2)

Fig. 16. (1) Dependences of the molar extinction coefficient $\bar{\varepsilon}$(●), the fluorescence intensity E(○: arbitrary units), and λ^4 (△: arbitrary units) of aluminium Calcein Blue on pH. (2) Dependences of the threshold excitation intensity (arbitrary units, ---: calculated value, ○: experimental values) and lasing wavelength (□) of aluminium Calcein Blue on pH. Concentration of aluminium Calcein Blue (1 : 1 mixture): 10^{-3} mol/l.

dependence of the fluorescence intensity, E, the molar extinction coefficient at 337 nm, $\bar{\varepsilon}$, and λ^4 on the aluminium concentration in the Calcein Blue solution are shown in Fig. 15(1). The threshold excitation intensity of the aluminium-Calcein Blue mixture is calculated from the spectroscopic parameters and is shown in Fig. 15(2), along with the experimental values. The increase in $\bar{\varepsilon}$ upon the increase in the aluminium concentration compensates for the decrease in λ^4, and the threshold excitation intensity does not vary much. The calculated value agrees with the experimental value, and it is confirmed that the laser action of the coordination compound is not quenched by the metal ion. However, it is impossible to observe the laser action when a molar excess of aluminium is added in the Calcein Blue solution. This may be due to the scattering effect of aluminium hydroxide; it is known that aluminium hydroxide is formed in the region of pH 4.5—10, then the excess aluminium coagulates and disturbs the laser action more severely than it does the fluorescence.

The lasing wavelength of the aluminium-Calcein Blue mixture gradually shifts to shorter wavelengths as in the case of the fluorescence spectrum, as is shown in Fig. 15(2). In this way the lasing wavelength of this mixture can be modified by varying the aluminium concentration in the Calcein Blue solution.

The data of the fluorescence intensity E, the extinction coefficient $\bar{\varepsilon}$, and λ^4 at various pH values are shown in Fig. 16(1). From these spectroscopic parameters, the threshold excitation intensity of aluminium Calcein Blue was calculated; it is shown in Fig. 16(2). Both the experimental and the calculated values have two minima, and they are consistent. The minimum at pH 11 is due to the dissociation to a ligand and an ion. Above pH 12 the laser action was not observed, as in the case of Calcein Blue itself.

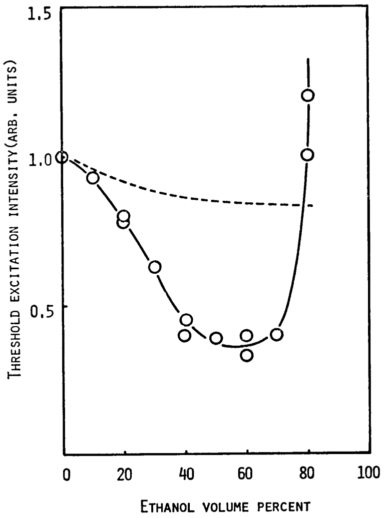


Fig. 17. Dependence of the threshold excitation intensity (arbitrary units) of aluminium Calcein Blue (10^{-3} mol/l) on the ethanol percent in the solvent (water). Solid curve: experimental values, broken curve: calculated value.

The wavelength of the laser emission of aluminium Calcein Blue is dependent on the pH. In order to modify the wavelength of the laser emission, it will be better to vary the pH than to vary the aluminium concentration, because the pH can be varied easily, for example, by adding a little acid or sodium hydroxide.

The threshold excitation intensity at various volume percentages of ethanol in the solvent was also calculated; the results are shown along with the experimental values in Fig. 17. Both the experimental and the calculated values decrease with an increase in the ethanol per-

Table 1. Characteristics of lasers of coordination compounds

Material	pH	λ_{las} (nm)	Threshold[a)]	Fluorescence intensity (E)[a)]	$\lambda_{fl}^4 E$	ε[b)]
C. B.	5	446	11	98	92	1.0
C. B.	12	—	no lasing	52	53	0.9
Al C. B.	5	418	11	104	75	1.5
Al C. B.	12	—	no lasing	54	54	0.9
Ca C. B.	5	446	11	96	90	—
Ca C. B.	12	450	12	98	95	—
Sr C. B.	5	446	11	96	90	—
Sr C. B.	12	452	13	96	95	—
Ba C. B.	5	446	11	96	90	1.0
Ba C. B.	12	454	13	94	95	0.9
4 MU	10	453	10	100	100	1.6
POPOP	d)	423	4	89	68	3.7
Al C. B.	e)	418	4	122	88	1.5

Concentration: 10^{-3} mol/l. a) Relative value for 4 MU. b) ε: molar extinction coefficient($\times 10^4$). c) C. B.: Calcein Blue. d) solvent: dioxane. e) solvent: 60 percent ethanol in water.

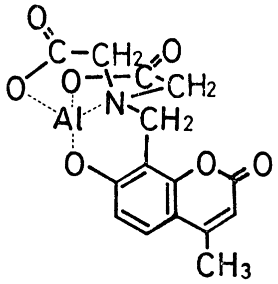


Fig. 18. The suggested structure of aluminium Calcein Blue. The aluminium ion is surrounded by a phenolic oxygen atom, two calboxylic oxygen atoms, and a nitrogen atom of iminodiacetic acid; however, the figure does not specify the number of the hydrogen atom attached to oxygen atoms and the coordination number of the aluminium atom.

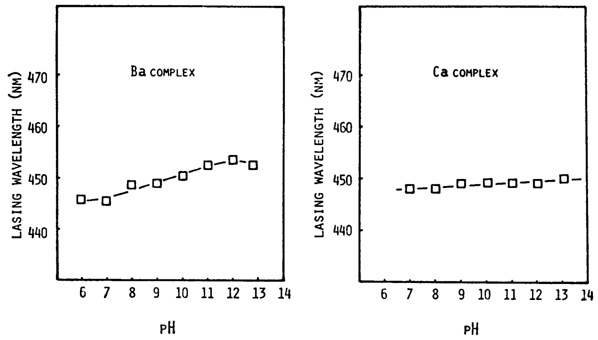


Fig. 19. Dependences of the lasing wavelength of calcium Calcein Blue (10^{-3} mol/l) and barium Calcein Blue (10^{-3} mol/l) on pH.

centage, as had been expected; however, the experimental value decreases more rapidly than does the calculated one. The variation in the refractive index in the mixture is small ($n_{D\,\mathrm{water}}=1.3330$, $n_{D\,\mathrm{ethanol}}=1.3618$) and can not induce the discrepancy. It may be due to the variation in the refractive index of the solution by heating by the irradiation of the nitrogen laser. However, the effect may not be large enough to induce such a large discrepancy. The steep increase in the threshold excitation intensity above 80 percent is due to the insolubility of the aluminium complex and to the light scattering in an ethanol–water mixture.

It has been reported that the lasing wavelength of 4-methylumbelliferone is modified in a water–ethanol mixture by an exciplex formation. In the case of an aluminium complex, the spectrum and the lasing wavelength in a water–ethanol mixture are close to those in water.

The structure of the aluminium Calcein Blue complex is suggested to be as is indicated in Fig. 18, since (1) the results of the continuous variation and mole ratio plots indicate the formation of a 1 : 1 complex between aluminium and Calcein Blue, (2) aluminium Calcein Blue should have a more rigid structure than Calcein Blue, as its quantum efficiency is larger than that of Calcein Blue, and (3) the phenolic oxygen coordinates with the aluminium ion since the phenolic electron does not take part in the resonance of the π electrons in the molecule, as the fluorescence spectrum does not shift to longer wavelengths. In this structure the aluminium ion is surrounded not only by a nitrogen atom but also by one phenolic and two carboxylic oxygen atoms, and binds the side chains. The structure of aluminium Calcein Blue is more rigid than that of Calcein Blue, in which neither of the side chains (CH_2COO^-) is bound.[17)] The formation of such rigid rings in the molecule increases the quantum yield of the material and reduces the threshold excitation intensity.

Laser Emission of Barium and Calcium Calcein Blue. The threshold excitation intensity of the alkali earth complex was calculated. Though the calcium complex lased up to pH 13.5, as had been expected from the calculated value, no quantitative comparison was carried out since the complex decomposed rapidly in high pH solution.

The effects of pH on the lasing wavelengths of barium and calcium Calcein Blue are shown in Fig. 19. The lasing wavelength of the barium complex can be modified by increasing the pH; however, that of calcium Calcein Blue can be modified only a little.

Laser Emission of Zirconium Calcein Blue. It has been reported that a zirconium ion is able to form a coordination compound with Calcein Blue at pH 5.[11] However, the laser action of this compound was not observed, since the intensity of the fluorescence was not strong and the light scattering by zirconium hydroxide disturbed the laser action at the concentration of 10^{-3} mol/l.

Laser Characteristics of Coordination Compounds. The characteristics of the lasers of the coordination compounds of Calcein Blue and dyes at 10^{-3} mol/l are listed in Table 1. Aluminium Calcein Blue at pH 12 and barium, strontium, and calcium Calcein Blue at pH 5 were identical to Calcein Blue in the threshold, in the wavelength, and in the intensity of the fluorescence band. This may indicate that no coordination compound is formed. The aluminium complex at pH 5 has the most intense fluorescence, and it is an excellent lasing material. The contribution of λ^4, however, does not induce the reduction of the threshold excitation intensity, since the laser emission occurs in the near UV region. Barium, strontium, and calcium complexes at pH 12 have relatively high thresholds compared with Calcein Blue and 4-methylumbelliferone. Though the fluorescence intensity of the POPOP is rather small, the threshold excitation intensity is relatively low, probably because of the large molar extinction coefficient and the solvent effect. The aluminium complex is considered to be superior to POPOP as a laser material, because of (1) the smaller intramolecular loss, since the quantum efficiency is larger (this would be significant for long-pulse excitation), (2) the better tuning capability (the laser action of POPOP is superradiation at 10^{-3} mol/l), (3) the variation in the lasing wavelength by the chelate reaction, and (4) the higher solubility in water. Furthermore, the threshold excitation intensity of an aluminium complex can be reduced by dissolving it in a water–ethanol mixture as low as that of POPOP at the same concentration.

Aluminium Calcein Blue lases in a month from preparation, and it is stable enough for practical use. However, the complex with the alkali earth metal ion in a high pH solution (above pH 13) decomposes in several hours. Calcein Blue can be easily recovered as precipitates from the complex solution by making the solution acidic.

Conclusion

The threshold excitation intensity of the organic liquid laser under a short-pulse excitation can be calculated by means of a simple equation by using its spectral parameters, such as the wavelength of the fluorescence emission at the maximum intensity, the fluorescence intensity, the concentration, and the molar extinction coefficient. The equation has been applied to the coordination compounds of Calcein Blue and found to be useful for the estimation of the lasing capability of a new material.

The coordination compounds of Calcein Blue have interesting characteristics as laser material; the lasing wavelength is easily modified by the complex formation and dissociation reactions, they are soluble in water, and their threshold values are low enough for practical use, since the quantum yield is near unity as a result of the ring formation. The complex with aluminium lases very efficiently at a shorter wavelength than any other efficiently-lasing coumarin derivatives and is stable enough for practical use. Thus, the coordination compound is proved to be a useful laser material.

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