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THE LUMINESCENCE SYSTEM OF YTTRIUM(III)–BPMPHD–CTMAB AND THE DETERMINATION OF YTTRIUM(III)

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Summary—The study indicated that yttrium(III) could form an ion association compound with a new synthetic reagent, 1,6-bi(1′-phenyl-3′-methyl-5′-pyrazolone-4′-)hexanedione (BPMPHD) and cetyl trimethyl ammonium bromide (CTMAB). The compound could enhance the natural fluorescence of BPMPHD by about 260 times, upon which a new fluorescence method was developed for determining yttrium in rare earth (RE) samples. The determination range was 9–900 ng/ml. The detection limit was 1.8 ng/ml. The composition of the ion association was $[Y(BPMHD)_2]^-CTMAB^+$.

The fluorescence of Y^{3+} upon itself in solution is not observed, but after complexing with an organic ligand with a chromophore, Y^{3+} makes the ligand, which has no fluorescence or has weak fluorescence, emit strong fluorescence. Thus fluorimetric determination methods of yttrium have been proposed.[1–13] Some of the methods involve extraction[3–5,7–9] and some of them are unstable with regard to time or the reagents decompose under the action of the uv light.[1,5,8] We found that Y^{3+} could form a ternary ion association compound, which emitted the Y^{3+}-perturbated fluorescence of the ligand, with the new synthetic reagent BPMHD[14] and CTMAB. The determination method proposed in this paper can be used down to 9 ng/ml, so it is more sensitive than most of the methods reported previously. The proposed method is fast and easily applied and the complex formed shows an adequate stability for at least 30 h.

EXPERIMENTAL

Apparatus

All fluorescence intensities were measured on a 850-fluorescence spectrophotometer (Hitachi, Japan). All absorption spectra were measured on a UV-240 spectrophotometer (Shimadzu, Japan).

Reagents

All the reagents were of analytical-reagent grade and distilled, deionised water was used. Stock standard solutions ($1.00 \times 10^{-2} M$) of RE ions were prepared by dissolving the corresponding oxides (99.9%) in hydrochloric acid and diluting with distilled water. BPMPHD solution ($1.0 \times 10^{-3} M$) was prepared by adding the appropriate amount of BPMPHD solid to 95% (v/v) ethanol solution, and dripping 1:1 $NH_3 . H_2O$ until BPMPHD dissolved completely. Aqueous CTMAB solution ($1.0 \times 10^{-2} M$) was used. Hexamethylenetetramine (HMTA)–HCl solution (10%, w/w) was used as a buffer, the pH being adjusted to 5.5 with hydrochloric acid.

Procedure

To a 25-ml test-tube, standard solutions of RE ions, CTMAB, BPMPHD and buffer solutions were added in that order. The mixture was diluted to 10 ml with distilled water and allowed to stand for 20 min. The fluorescence intensity was measured in a 1-cm quartz cell with excitation and emission wavelengths of 295 and 446 nm, respectively.

RESULTS AND DISCUSSION

Fluorescence spectra

The excitation and emission spectra of BPMPHD(1), Y–BPMPHD(2) and Y–BPMPHD–CTMAB(3) systems are shown in Fig. 1. From Fig. 1, it can be seen that after adding Y^{3+} or Y^{3+} and CTAB to the BPMPHD solution the fluorescence spectra hardly changed in shape or

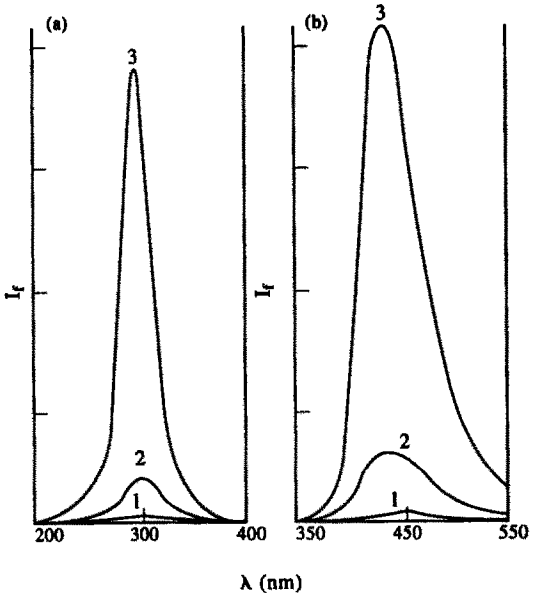

Fig. 1. Fluorescence spectra (a) excitation (λ_{em} = 446 nm) (b) emission (λ_{ex} = 295 nm). 1, BPMPHD; 2, Y–BPMPHD; 3, Y–BPMPHD–CTMAB. Conditions: BPMPHD, $3.5 \times 10^{-5} M$; Y^{3+}, $1.0 \times 10^{-5} M$; CTMAB, $2.0 \times 10^{-3} M$; pH 5.5.

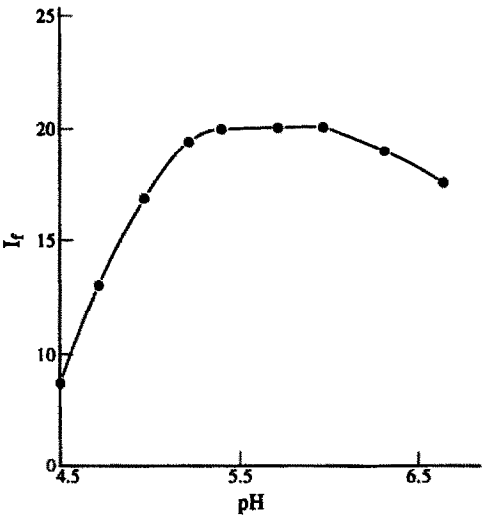

Fig. 2. Effect of pH. Conditions: Y^{3+}, $1.0 \times 10^{-6} M$; BPMPHD, $3.5 \times 10^{-5} M$; CTMAB, $2.0 \times 10^{-3} M$.

wavelength shift. The excitation and emission peaks were at 295 and 446 nm, respectively. However, the fluorescence intensity was enhanced by about 30 times and 260 times, respectively.

Factors affecting the fluorescence intensity

*p*H. The effect of pH on the fluorescence intensity of the system is shown in Fig. 2. It shows that the maximum intensity is reached in the range of pH 5.3–6.0. Experiments indicated that the addition of 1.0 ml HMTA–HCl solution of pH 5.5 was suitable.

BPMPHD concentration. The effects of the BPMPHD concentration on the fluorescence intensity of the systems containing $1.0 \times 10^{-5} M$ or $1.0 \times 10^{-6} M$ of Y^{3+}, were studied. Tests indicated that the fluorescence intensity increased BPMPHD concentration up to 3.0×10^{-5} and $2.5 \times 10^{-5} M$, respectively, remaining constant until $4.0 \times 10^{-5} M$. When the BPMPHD concentration was higher than $4.0 \times 10^{-5} M$, the intensity decreased slowly. In our experiments the BPMPHD concentration was fixed at $3.5 \times 10^{-5} M$.

Surfactants. Different kinds of surfactants have different effects on the fluorescence intensity of the system as shown in Table 1. The non-ionic and some cation surfactants have an enhancing effect, among which CTMAB has the greatest effect. CTMAB was selected as a surfactant in our experiments. The effects of its concentration on both the fluorescence intensity and the surface tension of the system are shown in Fig. 3. It can be seen that when the concentration of CTMAB was less than $0.1 \times 10^{-3} M$, the fluorescence intensity increased sharply with increase in CTMAB concentration, and then

Table 1. Effect of surfactants

Surfactant	Relative fluorescence intensity
No surfactant	1.0
CTMAB	8.0
OP	3.0
Sodium dodecyl sulfonate	2.2
Triton X-100	2.0
Octadecyl dimethyl ammonium acetate chloride	2.0
Tween-85	1.2
Arabic gum	1.2
β-Cyclodextrin	0.7
Hexadecyl pyridiniumbromide	0.1
Hexadecyl pyridiniumchloride	0.1
Tetradecyl pyridiniumbromide	0.1
Sodium dodecyl sulfate	0.1

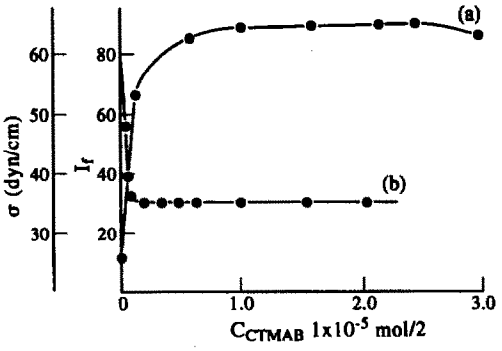

Fig. 3. Effect of CTMAB concentration on the fluorescence intensity and the surface tension of the system. (a) The fluorescence intensity curve, (b) the surface tension curve conditions: Y^{3+}, $5.0 \times 10^{-6} M$; BPMPHD, $3.5 \times 10^{-5} M$; pH 5.5.

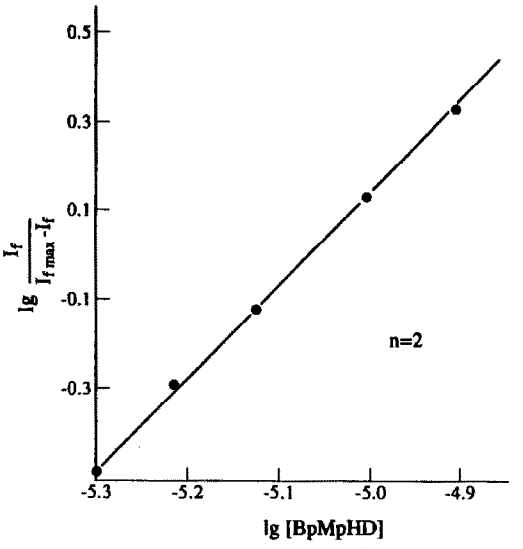

Fig. 4. Determination of n in the complex Y(BPMPHD)$_n$(CTMAB)$_m$ using balance change method. Conditions: Y^{3+} $5.0 \times 10^{-6} M$; pH 5.5.

tended to be constant reaching a maximum in the range of CTMAB concentration 1.25×10^{-3}–$2.25 \times 10^{-3} M$. From the curve of surface tension it can be seen that the surface tension first decreased sharply with increase of CTMAB concentration, reached a minimum and remained constant, $0.1 \times 10^{-3} M$ may be regarded as the apparent critical micelle concentration of CTMAB in the system. The fact that the fluorescence intensity of the system changed most when CTMAB was at its apparent critical micelle concentration illustrates that the formation of micelles had a great effect on the increase of the fluorescence intensity of the system. In our experiments the CTMAB concentration was fixed at $2.0 \times 10^{-3} M$.

Stability test. At room temperature the fluorescence intensity of the Y–BPMPHD–CTMAB system reached a maximum after 30 min and remained stable at least for 30 h. It can be concluded that the system is very stable.

Common cations and other lanthanides. The interference tests indicated that at $1.0 \times 10^{-5} M$ Y^{3+}, 100 times molar excess of Na^+, K^+, Ag^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Ba^{2+}, Ni^{2+}, Cd^{2+} and Cr^{3+} had no effect on the fluorescence intensity of the system. Al^{3+}, Fe^{3+} and Cu^{2+} seriously interfered. The highest concentrations causing 5% relative error in the fluorescence intensity were $5.0 \times 10^{-6} M$, $5.0 \times 10^{-7} M$ and $5.0 \times 10^{-7} M$, respectively. The effect of other lanthanides were examined when Y^{3+} concentration was $5.0 \times 10^{-7} M$. The highest permissible molar excess of other lanthanides causing a $\pm 5\%$ relative error in the fluorescence intensity were as follows: 20-fold of Eu^{3+}, Pr^{3+}, Ho^{3+}, Nd^{3+}, Tm^{3+} and Er^{3+}, four-fold of Ce^{3+}, two-fold of Sm^{3+}, one-fold of Tb^{3+} and Dy^{3+}, 0.5-fold of Yb^{3+} and Gd^{3+}, 0.2-fold of La^{3+}, 0.1-fold of Lu^{3+}.

Calibration curve and determination limit

Under optimum conditions, there was a satisfactory linear relationship between fluorescence

Table 2. Methods for the fluorimetric determination of Y(III)

Reagent	Application interval ($\mu g/ml$)	Reference
Salicylaldehydesemicarbazide	0.2–5.0	1
Rhodamine B + 3,5-diiodosalicylic acid	0.004*	3
Rhodamine B + 5,7-dinitro-8-hydroxyquinoline	0.05–0.8*	4
8-Hydroxyquinoline	0.2–1.0*	5
	0–0.5	6
2,4-Dihydroxybenzaldehydesemicarbazone	0.04–1.2	2
5,7-Dichloro-8-hydroxyquinoline	up to 0.2*	7
5,7-Dibromo-8-hydroxyquinoline	0.08–1.6*	8
Bis(8-hydroxy-2-quinolyl)methylamine	0.05–0.8	
	0.01–1.5*	9
	0.002 (detection limit)	10
1-Hydroxy-2-carboxyanthraquinone	0.01–0.8	11
Carbohydrazone	0.075–0.6	12

*Extraction fluorimetric method.

Table 3. Recovery test of Y(III) in Sm(III) matrix

Y(III) added (*ng*)	Y(III) found (*ng*)	Recovery ± RSD*(%)
177.8	177.8, 177.0, 175.0, 174.0, 173.3	98.7 ± 0.96
266.7	266.1, 265.2, 266.3, 267.0, 264.0	99.6 ± 0.60
355.6	355.0, 354.1, 355.2, 356.0, 354.0	99.8 ± 0.33

*Relative standard deviation.

Table 4. Determination of Y(III) in synthetic samples

Synthetic sample (*ng/ml*)	Y(III) found (*ng/ml*)	Average (*ng/ml*)	RSD (%)
Eu(III)15.7 Pr(III)14.1 Ce(III)1.40 La(III)0.139 Y(III)8.89	8.80, 8.70, 8.85, 8.76, 8.77	8.78	0.19
Sm(III)15.0 Yb(III)17.3 Nd(III)7.21 Y(III)44.5	44.5, 44.0, 44.3, 43.8, 43.9	44.1	0.29

intensity and Y^{3+} concentration in the range 9–900 ng/ml. The detection limit (signal-to-noise ratio = 2) was 1.8 ng/ml. Table 2 shows the methods proposed for the fluorimetric determination of Y^{3+}. It can be seen that the method proposed in this paper is the most sensitive.

Recovery test and determination

The standard addition method was used for the recovery test. The average recovery of Y^{3+} in the matrix of Sm^{3+} was in the range 98–101% as shown in Table 3. Therefore, the standard addition method is suitable for the determination of Y^{3+} in samples. We determined the amount of Y^{3+} in two synthetic samples using this method (see Table 4). It can be seen that the results are satisfactory.

In addition, we determined the amount of Y^{3+} in a national standard ore sample using this method and some reported methods of the same type. The results are shown in Table 5. We compared our method to the methods in Refs 6 and 11 with regard to accurity and precision; the results obtained by our method are more satisfactory. (The preparation of sample was as follows: weigh 0.5 g ore sample into a breaker of polytetrafluoroethylene, add 10 ml hydrogen fluoride into it and heat in order to remove silicon, then dissolve Al_2O_3 in NaOH solution. Filter out the final residuum and dissolve it in hydrochloric acid. Heat until nearly dry, then dilute with distilled water, pH being adjusted to 4–5 with NaOH. Filter out $Fe(OH)_3$ and $Fe(OH)_2$ and dilute the filtrate to 50 ml with distilled water).

Composition of the complex

Tests showed that an association compound $Y(BPMPHD)_n(CTMAB)_m$ was formed in the system. The composition of the complex was determined using the equilibrium shift method and the molar ratio method (Figs 4 and 5). The composition was 1:2:1 for Y:BPMPHD:CTMAB. The probable structure of the compound is as shown.

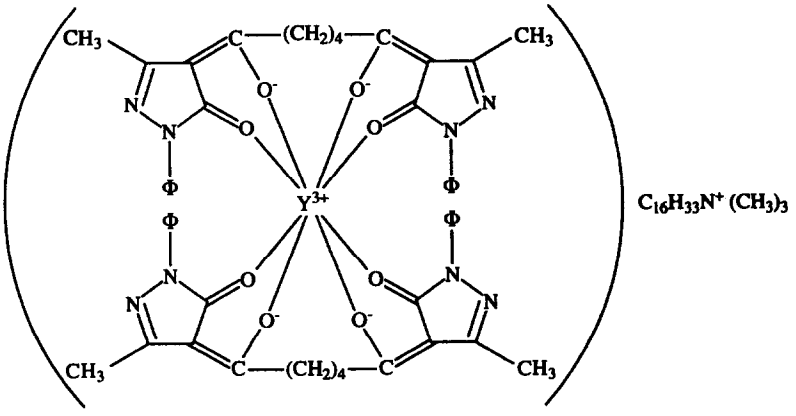

Table 5. Determination of Y^{3+} in a national standard ore material

Reagent	Reference	Y found (%)	mean (%)	RSD (%)
BPMPHD	this paper	0.0064, 0.0068, 0.0062, 0.0063, 0.0064	0.0064	3.6
8-Hydroxy-quinoline	6	0.0052, 0.0060, 0.0059, 0.0054, 0.0050	0.0055	4.4
1-Hydroxy-2-carboxyanthraquinone	11	0.0070, 0.0069, 0.0078, 0.0062, 0.0074	0.0071	6.0

The main components of the sample (%): SiO_2 72.83, Al_2O_3 13.40, Fe_2O_3 2.14, FeO 1.03, MgO 0.42, CaO 1.55, Na_2O 3.13, K_2O 5.01, Tm 0.000106, Mn 0.0463, Y 0.0062, P 0.0405, Sm 0.00097, Sc 0.0061.

The apparent association constant of $[Y(BPMPHD)_2]^-$ was examined using the molar ratio method and the continuous variation method. The results were 2.0×10^{12} and 1.99×10^{12} l^2/mol^2, respectively.

Luminescence mechanism

Experiments showed that either Y^{3+} or CTMAB had no fluorescence. From Fig. 1 it can be seen that by adding both Y^{3+} and CTMAB to the BPMPHD solution, the fluorescence intensity of system increased by about 260 times, while the fluorescence spectra had basically no change in shape or wavelength shift, which indicates that the fluorescence of the system belongs to Y^{3+}-perturbed fluorescence of ligand. The absorption spectra (Fig.6) shows that after BPMPHD complexed with Y^{3+} and CTMAB its absorption peak (at 260 nm) changed to long wavelength (268 nm), but its absorption intensity increased very little, so we conclude that the remarkable enhancement of the BPMPHD fluorescence after the addition of Y^{3+} and CTMAB occurred mainly because the formation of ion association compound can greatly increase the fluorescence quantum yield.

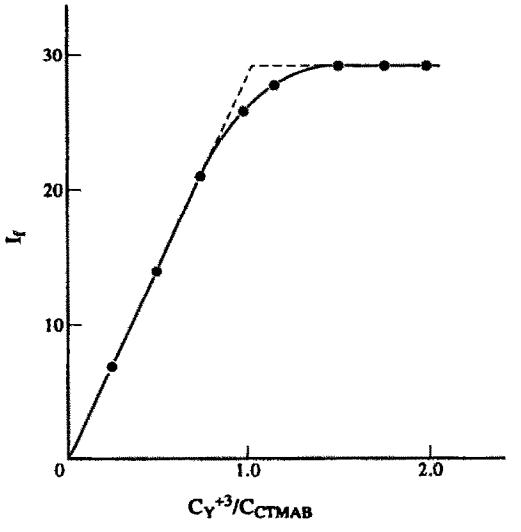

Fig. 5. Determination of m in the complex $Y(BPMPHD)_n(CTMAB)_m$ using the molar ratio method. Conditions: BPMPHD, 3.5×10^{-5} M; pH 5.5.

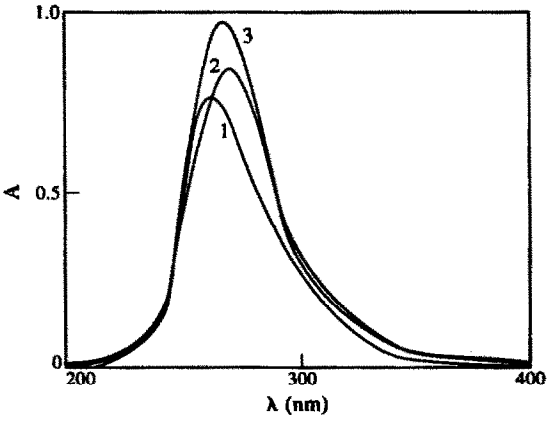

Fig. 6. Absorption spectra. 1, BPMPHD; 2, Y–BPMPHD; 3, Y–BPMPHD–CTMAB.

We think that the reason for the fluorescence enhancement of the system is as follows: (a) BPMPHD is a heterocyclic compound containing atoms of oxygen and nitrogen and a large conjugate π-bond structure which emits very weak fluorescence (350–550 nm). Y^{3+} has an empty $4f$ shell and does not emit fluorescence itself, but after complexing with BPMPHD, a compound with four quinary rings are formed, the rigid plane structure of BPMPHD is strengthened and the absorption cross-section of BPMPHD is enlarged, so the fluorescence quantum yield increases. (b) The ion association compound $[Y(BPMPHD)_2]^-$ $CTMAB^+$ can be dissolved in the CTMAB micelle and decreases the energy loss of the excited state of BPMPHD caused by colliding with the solvent molecules (H_2O), so increases the fluorescence quantum yield.

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