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Copper(II)-2,2′-Bipyridine-Eriochrome Cyanine R Ternary Complex and Its Application to the Spectrophotometric Determination of Copper(II)

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Copper(II) ion reacted with 2,2′-bipyridine (bpy) and Eriochrome Cyanine R (ECR) to give one of two kinds of ternary complexes according to the amount of reagents in a weakly basic medium. The combining ratios of three components in the complexes were estimated to be Cu(II): bpy: ECR=1: 1: 2 and 1: 1: 1, respectively, the former having an absorption maximum at 515 nm and the latter at 550 nm. The color development of the 1: 1: 2 complex was utilized in the spectrophotometric determination of copper(II) at microgram level. The ternary complex gave a maximum absorbance at 515 nm in the pH range 10.2—10.6. Under optimum pH, 2,2′-bipyridine and Eriochrome Cyanine R concentrations, a linear relationship holds between the absorbance of the complex and copper(II) concentration up to 6×10^{-5} mol dm^{-3}. The apparent molar absorption coefficient at 515 nm is about 20400 dm^3 mol^{-1} cm^{-1}, corresponding to Sandell's sensitivity index of 0.003_1 μg cm^{-2}.

Eriochrome Cyanine R (ECR), sodium 2″-sulfo-5,5′-dimethyl-4-hydroxyfuchsone-3,3′-dicarboxylate, a dyestuff of the triphenylmethane series like Chromazurol S, has been used for the spectrophotometric determination of aluminium(III),[1–3] beryllium(II)[4,5] and scandium(III),[6] and others. While 2,2′-bipyridine (bpy) is a sensitive and selective reagent for iron(II),[7,8] it has been reported to form a 1: 2 complex with copper(I), and a 1: 3 complex with copper(II).[9]

In a previous paper, the formation reaction of Cu(II)–bpy–Chromazurol S mixed ligand complex and its application to the spectrophotometric determination of copper(II) was reported.[10]

The present paper deals with studies on the color reaction forming the ternary complex composed of copper(II), 2,2′-bipyridine and Eriochrome Cyanine R, which has a structure similar to that of Chromazurol S, and on the spectrophotometric determination of copper(II) by means of this ternary complex. The composition of the ternary complex as well as the fundamental conditions for the determination of copper(II) are discussed.

Experimental

Reagents. *Copper(II) Standard Stock Solution (1.00×10^{-2} mol dm^{-3})*: Copper metal (Purity: 99.99%) was dissolved in a small amount of dilute nitric acid, with heating, and the solution was evaporated nearly to dryness on a water bath. The residual contents were dissolved in water containing nitric acid, and the solution was diluted with water in a volumetric flask (nitric acid was added to make the final acidity 0.01 mol dm^{-3}).

Standard Solution: The stock solution was diluted as required.

2,2′-Bipyridine Solution (1.00×10^{-3} mol dm^{-3}): 2,2′-Bipyridine (Wako Pure Chemical Industries, Ltd.) was dissolved in water containing hydrochloric acid (final concentration of hydrochloric acid: 0.002 mol dm^{-3}).

Eriochrome Cyanine R Solution (2.00×10^{-3} mol dm^{-3}): Eriochrome Cyanine R (Merck & Co., Inc.) was dissolved in water containing hydrochloric acid (final concentration of hydrochloric acid: 0.008 mol dm^{-3}). The acidified Eriochrome Cyanine R solution was stable for at least 1 year.

Buffer Solution: A borate buffer solution was prepared by mixing 0.1 mol dm^{-3} solution of borax and 0.2 mol dm^{-3} solution of hydrochloric acid or sodium hydroxide.

Triton X-100 Solution (1%, v/v): This was prepared by diluting polyethylene glycol mono[*o*-(1,1,3,3-tetramethylbutyl)phenyl]ether (BDH Chemicals Ltd.) with water.

All the other reagents were of analytical reagent grade. Doubly distilled water was used.

Apparatus. A Hitachi model 124 double-beam recording spectrophotometer and a Hitachi 139 spectrophotometer were used for measuring absorbance in glass cells of 10-mm pathlength. Measurements were carried out at 25±0.1 °C.

A Hitachi-Horiba model F-7 glass electrode pH meter was used for pH measurements.

Standard Procedure. An aliquot of a standard copper(II) solution was transferred to a 25-cm^3 volumetric flask, and then 2,2′-bipyridine and Eriochrome Cyanine R solutions were added. The flask was filled up to about 10 cm^3 by adding water. The pH value was adjusted with a buffer solution, the ionic strength of the solution being controlled to 0.1 with the amount of buffer solution. The total volume of the solution was made up to the mark with water. After gentle mixing, the absorbance of the resulting solution was measured against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. Suk and Mikeťuková[11] reported that Eriochrome Cyanine R dissociates in aqueous solution as follows:

$$\mathrm{H_5ECR^+} \rightleftarrows \mathrm{H_4ECR^0} \rightleftarrows \mathrm{H_3ECR^-} \rightleftarrows \mathrm{H_2ECR^{2-}} \rightleftarrows \mathrm{HECR^{3-}} \rightleftarrows \mathrm{ECR^{4-}}$$

The absorption spectra of each species caused by the acid dissociation of Eriochrome Cyanine R in aqueous medium are shown in Fig. 1. No spectrum of the neutral species H_4ECR^0 is shown, since it is almost insoluble in water. In the reaction, mainly the $HECR^{3-}$ species takes part in the color development.

The absorption spectra of the reagent blank (bpy and ECR) and the ternary complex with copper(II) at pH 10.4 are shown in Fig. 2. For the sake of comparison the spectrum of Cu(II)–ECR binary complex at the same pH value is also given. The absorption spectrum of the reagent blank (Curve 1) coincides with that of Eriochrome Cyanine R itself. Thus it seems that there is no interaction between Eriochrome Cyanine R and 2,2′-bipyridine. The maximum absorption wavelengths of both the binary and the ternary complexes are found

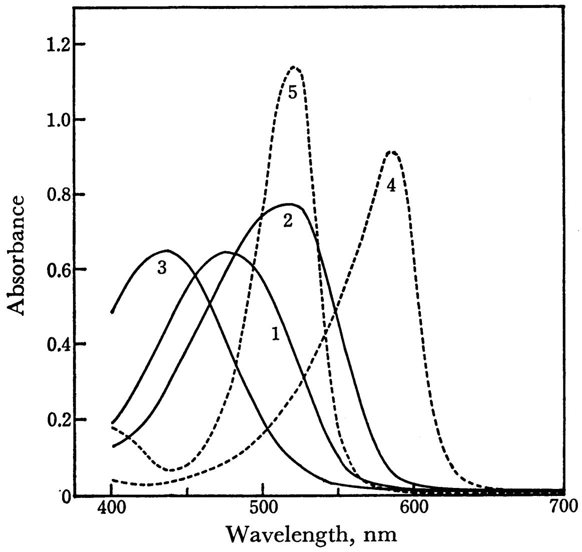

Fig. 1. Absorption spectra of Erichrome Cyanine R at various acidities.
Concn of ECR—1, 2 and 3: 6.0×10^{-5} mol dm^{-3}, 4 and 5: 3.0×10^{-5} mol dm^{-3}; acidity—1: pH 1.35 (H_3ECR^-), 2: pH 3.50 (H_2ECR^{2-}), 3: pH 9.00 ($HECR^{3-}$), 4: pH 13.5 (ECR^{4-}), 5: 9 mol dm^{-3} H_2SO_4 (H_5ECR^+).

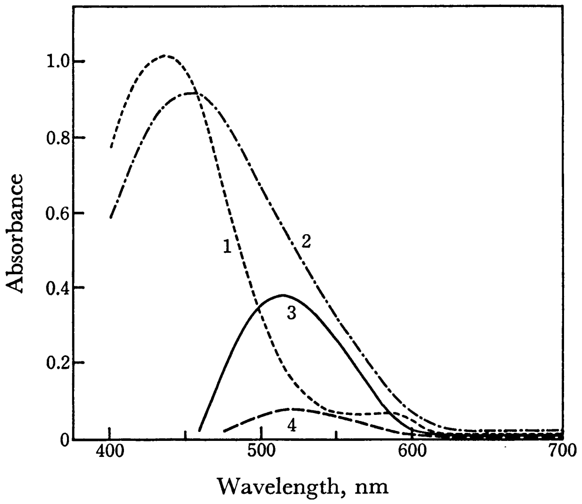

Fig. 2. Absorption spectra of Cu(II)-bpy-ECR complex and binary Cu(II)-ECR complex.
Concn of Cu(II), bpy and ECR: 2.0×10^{-5} mol dm^{-3}, 4.0×10^{-5} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3}, respectively; pH: 10.4, ionic strength: 0.1; 1: reagent blank *vs.* water, 2: Cu(II)-bpy-ECR *vs.* water, 3: Cu(II)-bpy-ECR *vs.* reagent blank, 4: Cu(II)-ECR *vs.* ECR.

at about 515 nm. The addition of 2,2′-bipyridine to the Cu(II)-ECR complex gives rise to a large hyperchromic shift at the maximum absorption wavelength. The hyperchromic effect is probably due to the increment of molecular cross section caused by the combination with 2,2′-bipyridine. It follows that the sensitivity of the color development increases remarkably (about 5-fold).

The absorption spectra of colored solutions at different pH values were measured against the reagent blanks (Fig. 3). At pH above 10, the maximum absorption wavelength is found at 515 nm, the spectra showing similar shapes. At pH below 10, each peak is shifted toward a longer wavelength, and at pH below 9.5, a part of the formed complex precipitates, even in the presence of Triton X-100 (0.04%).

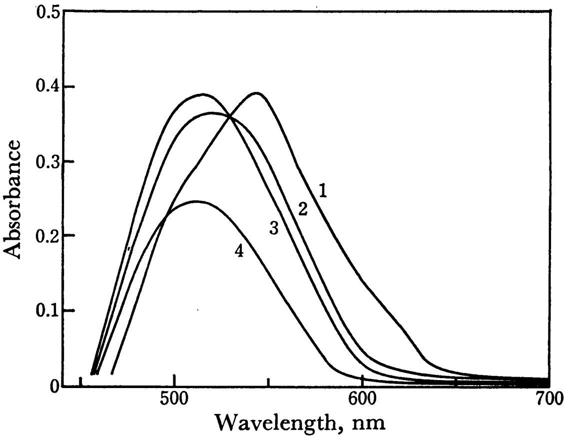

Fig. 3. Absorption spectra of Cu(II)-bpy-ECR complex at various pH values.
Concn of Cu(II), bpy and ECR: 2.0×10^{-5} mol dm^{-3}, 4.0×10^{-5} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3}, respectively; Triton X-100: 0.04%, ionic strength: 0.05; 1: pH 9.60, 2: pH 10.00, 3: pH 10.31, 4: pH 11.15.

The concentration of Eriochrome Cyanine R was kept constant and varying amounts of an equimolar mixed solution of copper(II) and 2,2′-bipyridine were added. The absorption spectra were measured against the water blank. The results for pH 10.4 are shown in Fig. 4.

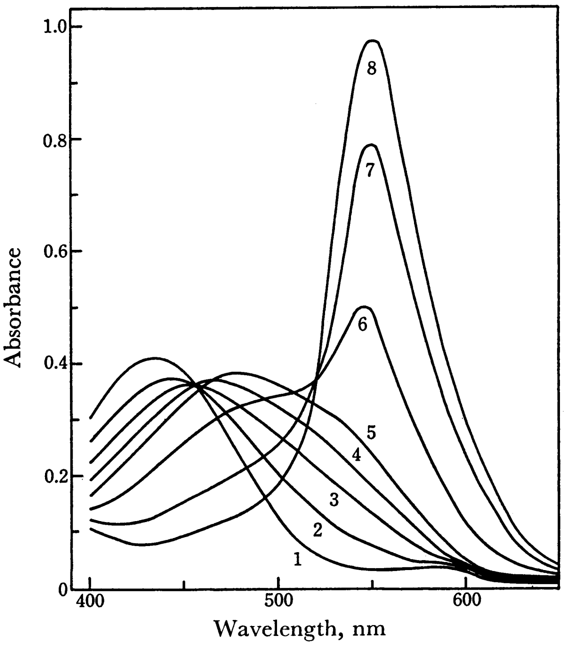

Fig. 4. Absorption spectra of Cu(II)-bpy-ECR system.
Concn of ECR: 4.0×10^{-5} mol dm^{-3}; pH: 10.4, Triton X-100: 0.04%, ionic strength: 0.05; each concn of Cu(II) and bpy (mol dm^{-3})—1: 0, 2: 5.0×10^{-6}, 3: 1.0×10^{-5}, 4: 1.5×10^{-5}, 5: 2.0×10^{-5}, 6: 3.0×10^{-5}, 7: 4.0×10^{-5}, 8: 5.0×10^{-5}.

Under the conditions of excess copper(II), a part of the complex formed precipitate. However, by addition of Triton X-100 the complex existed in a homogeneous dispersed state without formation of any precipitate. An absorption band appears with a maximum at 550 nm in accordance with the increasing amounts of the mixed solution of copper(II) and 2,2′-bipyridine, indicating that there are two absorbing species under these conditions (Fig. 4).

Composition of the Ternary Complexes. From the results given in Figs. 2 and 4, it seems that two kinds of complexes can be formed in a weakly basic pH medium (pH 10.4), according to the concentration ratio of the reagents.

A triangular coordinate method extended to three-component system of the continuous variation plot was applied to the determination of the composition of ternary complexes. The sum of the initial concentrations of copper(II), 2,2′-bipyridine and Eriochrome Cyanine R in the solution was kept constant, and preparation of the colored solution was carried out with 45 different compositions. The absorbance of the solution was measured against the reagent blank at 515 and 550 nm. The results are shown in Figs. 5 and 6, respectively. The contour lines in both figures show various compositions of equal absorbance. At 515 nm, maximum absorbance is obtained at the mole ratio of Cu(II) : bpy : ECR=0.25 : 0.25 : 0.5, namely 1 : 1 : 2 (Fig. 5). Similarly, at 550 nm, maximum absorbance is obtained at the mole ratio of Cu(II) : bpy : ECR= 1 : 1 : 1 (Fig. 6).

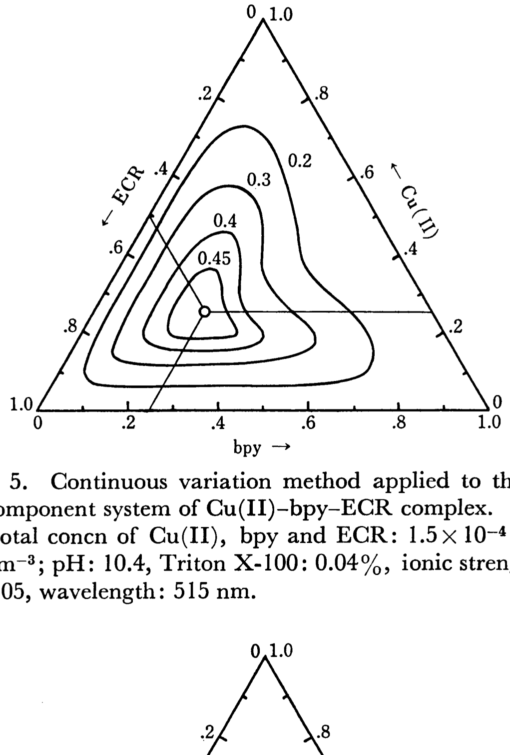

Fig. 5. Continuous variation method applied to three-component system of Cu(II)–bpy–ECR complex.
Total concn of Cu(II), bpy and ECR: 1.5×10^{-4} mol dm^{-3}; pH: 10.4, Triton X-100: 0.04%, ionic strength: 0.05, wavelength: 515 nm.

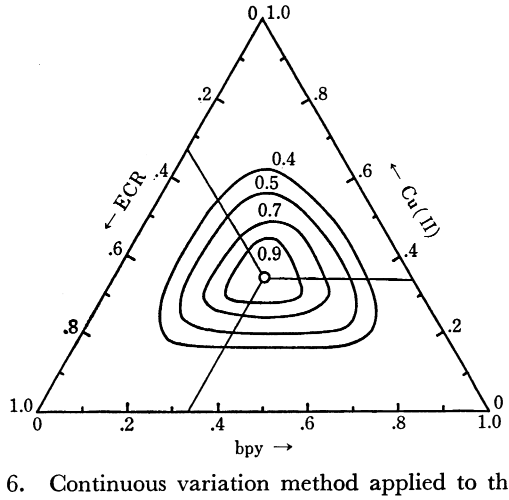

Fig. 6. Continuous variation method applied to three-component system of Cu(II)–bpy–ECR complex.
Wavelength: 550 nm; the other conditions except wavelength are the same as those in Fig. 5.

In the above experiments (Figs. 3, 4, 5, and 6) nonionic surfactant Triton X-100 was used as a solubilizing agent of the ternary complex. Addition of Triton X-100, however, had no effect on the light absorption of solutions.

From the results (Figs. 4, 5, and 6) it is evident that two types of ternary complex are formed successively, according to the amount of reagent, at pH 10.4, the combining ratio of Cu(II): bpy: ECR being confirmed to be 1: 1: 2 in one and 1: 1: 1 in the other. The maximum absorption wavelengths of the 1: 1: 2 and 1: 1: 1 complexes were 515 and 550 nm, respectively. In Cu(II)–bpy–Chromazurol S ternary complex[10] only the 1: 1: 2 species is formed.

The color development of the 1: 1: 2 complex with absorption maximum at 515 nm in a weakly basic pH medium was utilized in the spectrophotometric determination of copper(II). Conditions for the color development were investigated.

Effect of pH. The effect of pH on the color development of the ternary complex was studied with solutions adjusted to various pH values. The results are shown in Fig. 7. The maximum and nearly constant absorbance is obtained over the pH range 10.2—10.6.

Effect of 2,2′-Bipyridine and Eriochrome Cyanine R Concentrations. With the concentration of copper(II) kept constant, varying amounts of reagent were added, and the absorbances of the resulting solutions were measured against the reagent blanks. The results are shown in Fig. 8. When the concentration of 2,2′-bipyridine was varied and the concentrations of copper(II) and Erio-

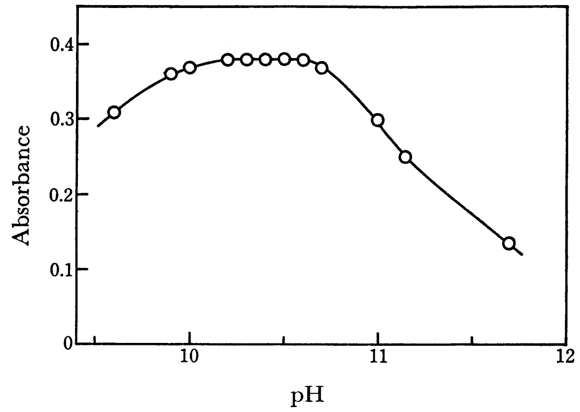

Fig. 7. Effect of pH on the absorbance of Cu(II)–bpy–ECR complex.
Concn of Cu(II), bpy and ECR: 2.0×10^{-5} mol dm^{-3}, 4.0×10^{-5} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3}, respectively; ionic strength: 0.1, wavelength: 515 nm.

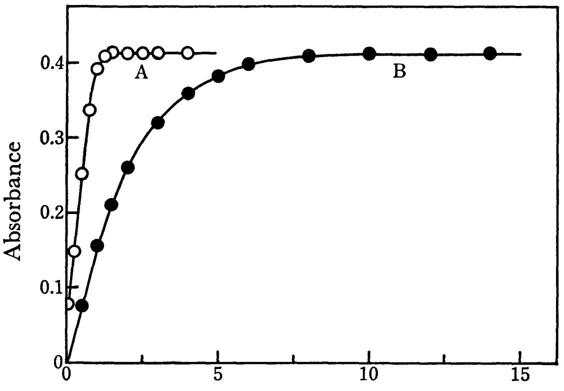

Fig. 8. Effect of 2,2′-bipyridine and Eriochrome Cyanine R concentrations on the absorbance of Cu(II)–bpy–ECR complex.
Concn of Cu(II): 2.0×10^{-5} mol dm^{-3}, pH: 10.4, ionic strength: 0.1, wavelength: 515 nm; A: [bpy]/[Cu(II)], ECR: 2.0×10^{-4} mol dm^{-3}, bpy varying; B: [ECR]/[Cu(II)], bpy: 4.0×10^{-5} mol dm^{-3}, ECR varying.

chrome Cyanine R were kept constant, the constant and maximum absorbance was obtained with a concentration ratio higher than 1.5-fold of 2,2′-bipyridine to copper(II) (Curve A). The absorbance at mole ratio of zero in curve A corresponds to that of the binary Cu(II)–ECR complex. In the same way, the effect of various Eriochrome Cyanine R concentrations is shown by curve B. More than 10-fold excess of Eriochrome Cyanine R over the copper(II) concentration is necessary in order to obtain the maximum color intensity.

Effect of Time. Color development of the ternary complex was almost instantaneous, the absorbance remaining unchanged for several hours.

Calibration Curve. A calibration curve was made under optimum conditions. A linear concentration–absorbance relationship is obtained in the copper(II) concentration up to 6×10^{-5} mol dm^{-3}. The regression equation of the calibration curve obtained by a least squares method is as follows:

$$\log (I_0/I) = 20433[\mathrm{Cu(II)}] + 0.005_5 \qquad (1)$$

Experimental conditions
bpy: 2.0×10^{-4} mol dm^{-3}
ECR: 5.0×10^{-4} mol dm^{-3}
pH: 10.4
Ionic strength: 0.1
Wavelength: 515 nm

Here, $\log(I_0/I)$ and [Cu(II)] are the absorbance of ternary complex against the reagent blank as reference and the concentration (mol dm^{-3}) of copper(II) in the solution, respectively. As is evident from Eq. 1, the apparent molar absorption coefficient of the complex is about 20400 dm^3 mol^{-1} cm^{-1}, corresponding to Sandell's sensitivity index of 0.003_1 μg cm^{-2}. When this is compared with indices of other similar ternary systems, its sensitivity is lower than that of the method using Neocuproine and Chromazurol S (0.002_2 μg cm^{-2}),[12] but comparable to that of the method using 2,2′-bipyridine and Chromazurol S (0.003_1 μg cm^{-2}).[10]

Effect of Diverse Ions. The influence of several cations which might introduce a large error in the determination of copper(II), and that of a few anions as masking agents were examined. The results are given in Table 1. All the cations interfere with the copper(II) determination. Beryllium(II), cobalt(II), nickel(II), and manganese(II) give high positive error, and iron(III) gives negative error. Tartrate, citrate and cyanide ions inhibit color formation of the ternary complex. Fluoride and phosphate ions, however, have almost no influence on the ternary complex formation, even in large amounts. Sodium fluoride and sodium phosphate can, therefore, serve as excellent masking agents. Among the coexisting cations in Table 1, metal cations except beryllium(II) and cobalt(II) can be effectively masked by using appropriate amounts of either fluoride or phosphate.[12,13]

Table 1. Influence of several foreign ions

Foreign ion	Ion added (μmol)	Absorbance[a] (515 nm)	Relative error (%)
	Nil	0.414	
Beryllium(II)	0.5	1.022	146.9
Cobalt(II)	0.5	0.542	30.9
Nickel(II)	0.5	0.484	16.9
Manganese(II)	0.5	0.457	10.4
Thorium(IV)	0.5	0.444	7.2
Aluminium(III)	0.5	0.417	0.7
Iron(III)	0.5	0.392	−5.3
Fluoride	50	0.416	0.5
	150	0.412	−0.5
	200	0.401	−3.1
Phosphate	5	0.409	−1.2
	25	0.397	−4.1
	50	0.393	−5.1
Tartrate	12.5	0.349	−15.7
	50	0.247	−40.3
Citrate	12.5	0.334	−19.3
	50	0.238	−42.5
Cyanide	2.5	0.030	−92.8
	5	0.011	−97.3

Copper(II) taken: 31.8 μg; a) Each result is the average of three separate analyses.

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