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Spectrophotometric Study on The Extraction of The Ternary Complex Composed of Cobalt(II), 8-Hydroxyquinoline-5-sulphonic Acid and Zephiramine

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8-Hydroxyquinoline-5-sulphonic acid (H_2QS) reacts with cobalt(II) in the presence of zephiramine (tetradecyl-dimethyl-benzyl-ammonium chloride) and gives a yellow green association complex. The ternary complex having an absorption maximum at 405 nm can be extracted into chloroform at pH 6.8—9.3. Beer's law holds for 2.73—33.0 μg of cobalt(II); molar absorptivity, 1.39×10^4 cm^{-1}mol^{-1}*l*. The composition of cobalt(II)-H_2QS complexes in water is 1: 1 at pH 4.4, 1: 2 at pH 5.8, and 1: 3 at pH 7.6. The composition of the ternary complex is estimated to be $[\mathrm{Co^{2+}(QS^{2-})_2(HQS^-)(Z^+)_3}]_o$. The equilibrium constant for the extraction

$$K=\frac{[\mathrm{Co^{2+}(QS^{2-})_2(HQS^-)(Z^+)_3}]_o}{[\mathrm{Co^{2+}}][(\mathrm{HQS^-Z^+})]_o^3[\mathrm{OH^-}]^2}$$

was determined. It was found that $\log K=29.01\pm1.86$.

The solvent extraction of the ion-pair formed by the interaction of 8-hydroxyquinoline-5-sulphonic acid-metal chelate anions with cation of zephiramine (tetradecyl-dimethyl-benzyl-ammonium chloride) has been applied to the spectrophotometric determination of iron(III),[1] nickel(II),[2] and copper(II).[3] Matsuo *et al.*[4] proposed the extraction of thiocyanatocobaltate(II) complex anion with zephiramine into chloroform. In this paper, fundamental conditions for the spectrophotometric determination of cobalt(II) and the composition of the ternary complex formed are discussed: 8-hydroxyquinoline-5-sulphonic acid (H_2QS) reacts with cobalt(II)[5,6] and gives a water soluble chelate, which can be extracted into chloroform in the presence of zephiramine (Z^+Cl^-). The intensity of the yellow green coloration with an absorption maximum at 405 nm in chloroform is proportional to the amount of cobalt(II) in the aqueous layer.

Experimental

Reagents. *Cobalt(II) Standard Solution*: 2.3795 g of cobalt chloride (Wako Chemicals Co., guaranteed reagent) was dissolved into 10 m*l* of hydrochloric acid and diluted to 1 liter with deionized water. The solution was standardized with EDTA-titration using murexide as an indicator, and found to contain 586 μg of cobalt(II) per m*l*. The solution was diluted as required.

H_2QS Solution: 1.00×10^{-3}M solution was prepared by dissolving H_2QS (Wako Chemicals Co.) into water.

Zephiramine Solution: 5.00×10^{-3}M solution was prepared by dissolving Dotite zephiramine into water.

Buffer Solutions: Acetate buffer solution, pH 3.4—5.6;

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[1] T. Kambara, S. Matsumae, and K. Hasebe, *Bunseki Kagaku*, **19**, 462 (1970).

[2] T. Kambara, M. Sugawara, and K. Hasebe, *ibid.*, **19**, 1239 (1970).

[3] T. Kambara, M. Maeyama, and K. Hasebe, *ibid.*, **20**, 1249 (1971).

[4] H. Matsuo, S. Chaki, and S. Hara, *ibid.*, **14**, 935 (1965).

[5] C. F. Richard, R. L. Gustafson, and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 1033 (1959).

[6] L. G. Sillén and A. E. Martell, Ed., "Stability Constants of Metal-Ion Complexes," The Chemical Society London (1964), p. 609.

Stock solutions of 0.1 M sodium acetate and 0.1 M acetic acid were prepared and mixed in appropriate proportions. Phosphate buffer solution, pH 6.3—8.3; Stock solutions of 0.1 M disodium phosphate dihydrate and 0.1 M potassium phosphate dibasic were prepared and mixed as required. Borate buffer solution, pH 9.1—10.5; 0.1 M borax solution was mixed with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

Chloroform and other reagents were all of analytical reagent grade.

Apparatus. Spectrophotometric measurements were carried out with a Shimadzu Model QV-5 spectrophotometer with 10-mm cells. The pH was measured with a Hitachi-Horiba, Model F-5, glass electrode pH meter. A shaker of Iwaki KM was used.

Established Procedure. Take 29.3 μg of cobalt(II) in a 100-m*l* separatory funnel and add 10 m*l* of the H_2QS solution and 3 m*l* of the zephiramine solution. Adjust pH to 7.3—7.5 with 15 m*l* of phosphate buffer solution and dilute to 50 m*l* with deionized water. Add 10 m*l* of chloroform, shake the mixture for 15 min and then allow the layers to separate for 10 min. Draw off the chloroform layer into a beaker containing anhydrous sodium sulphate and transfer the extract into a cell. Measure the absorbance at 405 nm against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. The absorption spectra of the aqueous layer and the organic extract obtained by the above procedure are given in Figs. 1 and 2, respectively. With increasing pH values, the absorption maxima of the cobalt(II)-H_2QS complexes in water shifted to longer wavelengths, *viz.*, 365 nm at pH 4.7, 370 nm at pH 5.3, and 375 nm at pH 7.9.

The ternary complex formed by the interaction of zephiramine with cobalt(II)-H_2QS complex anion had an absorption maximum at 405 nm both in the aqueous and organic layers (Figs. 1 and 2).

The bathochromic effect is probably due to the increment of molecular cross section caused by the combination with zephiramine. An ion-pair of H_2QS with zephiramine was also extracted but the absorbance at 405 nm was very low.

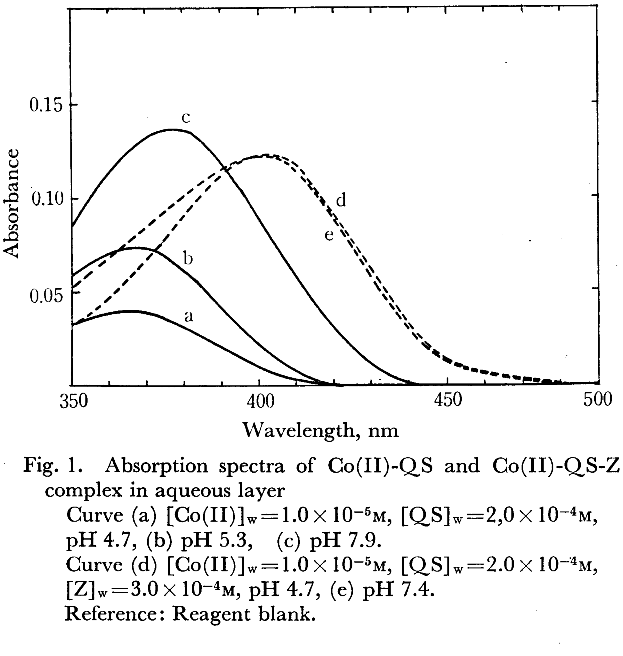

Fig. 1. Absorption spectra of Co(II)-QS and Co(II)-QS-Z complex in aqueous layer
Curve (a) $[Co(II)]_w = 1.0 \times 10^{-5}$M, $[QS]_w = 2{,}0 \times 10^{-4}$M, pH 4.7, (b) pH 5.3, (c) pH 7.9.
Curve (d) $[Co(II)]_w = 1.0 \times 10^{-5}$M, $[QS]_w = 2.0 \times 10^{-4}$M, $[Z]_w = 3.0 \times 10^{-4}$M, pH 4.7, (e) pH 7.4.
Reference: Reagent blank.

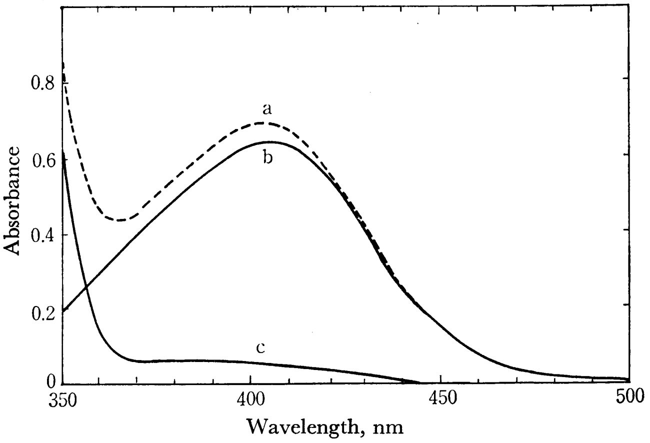

Fig. 2. Absorption spectra of the ternary complex Co(II)-QS-Z in chlorofrom
$[Co(II)]_w = 1.0 \times 10^{-5}$M, $[QS]_w = 2.0 \times 10^{-4}$M, $[Z]_w = 3.0 \times 10^{-4}$M, pH 7.4, Volume of aq. layer $V_w =$ 50 m*l*, Volume of org. layer $V_o = 10$ m*l*, Curve (a) *vs.* $CHCl_3$, (b) *vs.* reagent blank, (c) Reagent balnk *vs.* $CHCl_3$.

Effect of pH. The aqueous layer containing 29.3 μg of cobalt(II) was adjusted to various pH values and treated by the above procedure. It was found that the extraction of the ternary complex began at pH 3.0 and the pH range for the optimum extraction was 6.8—9.3 with phosphate and borate buffer solutions. Yamamoto[7] and Tôei[8] successfully employed nitrobenzene for the extraction of ion-pairs of tetracyanatonickelate-(II) anion with bis(1,10-phenanthroline)iron(II) chelate cation and alkaline metals with picrate anion, respectively. Extraction with nitrobenzene was carried out by the above procedure. The absorbance measurement was made at 430 nm, the wavelength of the absorption maximum of the nitrobenzene extract. The optimum pH range was 7.6—8.3.

Effect of H_2QS Concentration. With the concentrations of cobalt(II) and zephiramine kept constant, various amounts of H_2QS were added and extraction was carried out by the above procedure. The absorbance of the organic layer was found to be constant and maximum in the concentration range 7—30-fold mol of H_2QS to cobalt(II). However, H_2QS in concentration higher than 30-fold of cobalt(II) lowered the absorbance of the extract. Therefore, the H_2QS concentration was kept to 20-fold to cobalt(II).

Effect of Zephiramine Concentration. The zephiramine concentration was varied for a series of extractions while the cobalt(II) and H_2QS concentrations were kept constant. The absorbance of the extract was measured against the reagent blank. It was found that the optimum molar concentration of zephiramine lies in 20—40-fold of cobalt(II). Further addition of zephiramine increases the absorbance of the extract gradually. Thus the concentration of zephiramine was kept to 30-fold of cobalt(II) throughout the procedure.

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[7] Y. Yamamoto, T. Kumamaru, S. Miura, and S. Kimura, *Nippon Kagaku Zasshi*, **92**, 64 (1971).

[8] M. Yamane, T. Iwachido, and K. Tôei, This Bulletin, **44**, 745 (1971).

Effect of Shaking Time. The shaking time was varied from 30 sec to 30 min. Stable and constant absorbance of the extract was found for a shaking time longer than 10 min.

Extractability, Distribution Ratio, and Molar Absorptivity. Extractability under optimum conditions was determined by repetition of the extraction procedure on the same aqueous layer. A 50 m*l* portion of the aqueous layer containing 29.3 μg of cobalt(II) was shaken with 10 m*l* of chloroform. Twenty five milliliters of separated aqueous layer was again shaken with 5 m*l* of chloroform, followed by re-extraction on the 20 m*l* of the aqueous layer with 4 m*l* of chloroform. Absorbances A_1, A_2, and A_3 of each extract in sequence were measured. The extractability is then given by

$$E_{\max} = \frac{A_1}{A_1+A_2+A_3} \times 100$$
$$= \frac{0.650}{0.650+0.038+0.002} \times 100 = 94.2\%$$

where A_i is the absorbance of each extract at 405 nm. Thus, distribution ratio $D_{\max}$ is

$$D_{\max} = \frac{E_{\max}}{100-E_{\max}} \times \frac{V_w}{V_0} = 69.3$$

Molar absorptivity ε of the ternary complex calculated by using absorbance A_1 and $E_{\max}$ is

$$\varepsilon = 1.39 \times 10^4\ \mathrm{cm^{-1}\ mol^{-1}}\ l$$

The molar absorptivity is larger than 8500, that of the oxine complex $CoOx_2(C_4H_9NH_2)_2$.[9] In the case of the extraction with nitrobenzene, 98.5% of cobalt(II) was extracted by one extraction and the distribution ratio was 337.4. However, the molar absorptivity was 1.09×10^4.

Calibration Curve. Varying amounts of cobalt(II) were added to the aqueous layer and extraction was carried out. For the first extract, Beer's law holds for 2.73—33.0 μg of cobalt(II). Sandell's sensitivity for the absorbance of 0.001 is 0.0042 μg/cm². The relative standard deviation obtained by 7 measurements was 0.63% for the 29.3 μg of cobalt(II).

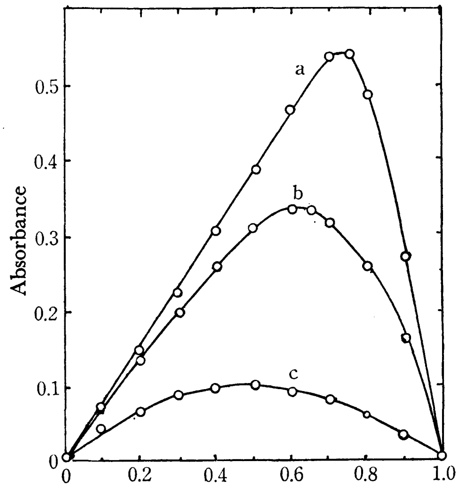

Fig. 3. Continuous variation method applied to Co(II)-H_2QS chelate in water
$[Co(II)]+[H_2QS]=2.00\times10^{-4}$M,
Curve (a) pH 7.6, Wavelength: 375 nm,
(b) pH 5.8, Wavelength: 370 nm,
(c) pH 4.4, Wavelength: 365 nm.

Composition of Cobalt(II)-H_2QS Complexes. The results of continuous variation method (Fig. 3) indicate that molar ratios of H_2QS to cobalt(II) are 1: 1 at pH 4.4, 2:1 at pH 5.8, and 3:1 at pH 7.6. The same results were obtained also by the mole ratio method. The results coincide with those by the potentiometric method.[5]

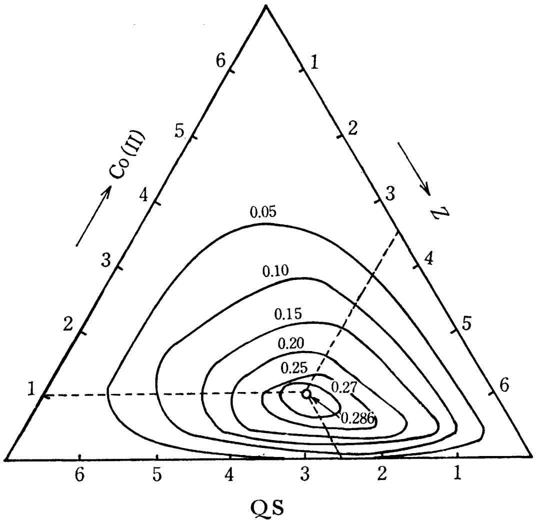

Fig. 4. Continuous variation method applied to the three-component system of Co(II)-QS-Z complex
$V_w=50$ m*l*, $V_o=10$ m*l*, $[Co(II)]_w+[QS]_w+[Z]_w=7.00\times10^{-5}$M, pH 7.4, Wavelength: 405 nm,
Reference: Chloroform,
Numerals show the absorbance of organic layer.

Composition of the Ternary Complex. Determination of the composition of the ternary complex in the organic layer was attempted by means of the triangular coordinate method for three-component system.[1-3] The sum of the initial concentrations of cobalt(II), H_2QS and zephiramine in the aqueous layer being kept to 7.00×10^{-5}M, extraction was carried out at 74 points of various compositions. The absorbance of the extract was measured against chloroform. The contours in Fig. 4 show a composition of equal absorbance. The maximum absorbance was obtained in the composition of cobalt(II): H_2QS: zephiramine=1: 2.5: 3.5. However, results of the continuous variation method applied to the system of the cobalt(II)-H_2QS complex in the presence of excess zephiramine indicated that the composition of the ternary complex was cobalt(II): H_2QS: zephiramine=1: 3: 3. The same result was also obtained by applying the mole ratio method. We see that the contour which indicates the absorbance of 0.050 partially overlaps the QS-axis (Fig. 4). Deviation of the triangular method from continuous variation and mole ratio methods therefore seems to be due to the effect of absorption by the ion-pair of H_2QS with zephiramine. Thus, the composition of the ternary complex was estimated to be $[Co^{2+}(QS^{2-})_2(HQS^-)(Z^+)_3]_o$.

Equilibrium Constant For Extraction of The Ternary

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[9] F. Umland, *Z. Anal. Chem.*, **190**, 186 (1962).

Complex. When the ternary complex is extracted into chloroform, the extraction equilibrium is given as follows:

$$\begin{aligned} &Co^{2+} + 3[(HQS^{-}Z^{+})]_o + 2OH^{-} \\ &\quad = [Co^{2+}(QS^{2-})_2(HQS^{-})(Z^{+})_3]_o + 2H_2O \qquad (1) \end{aligned}$$

where suffix o indicates the organic layer. The equilibrium constant K is given by

$$K = \frac{[Co^{2+}(QS^{2-})_2(HQS^{-})(Z^{+})_3]_o}{[Co^{2+}][(HQS^{-}Z^{+})]_o^3[OH^{-}]^2} \qquad (2)$$

The initial concentration of cobalt(II) in 50 ml aqueous layer is kept at *C, those of H_2QS and zephiramine at 3*C and the pH of the aqueous layer at 7.4, and the layer is shaken with 10 ml of chloroform. The absorbance of the organic layer is measured against chloroform after equilibrium is attained. The concentration of the ternary complex in the organic layer C_T is calculated from the molar absorptivity. Equation (2) is then expressed by

$$K = \frac{C_T}{\left[{}^*C - \frac{10}{50}C_T\right]\left[\frac{50}{10} \times 3{}^*C - 3C_T\right]^3[OH^{-}]^2} \qquad (3)$$

The results obtained with various values of initial concentration *C are shown in Table I. The logarithm of the equilibrium constant is 29.01±1.86.

Table 1. Equilibrium constant of Co(II)-QS-Z ternary complex shown by Eq. (1)—(3)

**C* (M)	Absorbance	C_T (M)	pH	log K
1.0×10^{-5}	0.256	1.84×10^{-5}	7.34	28.15
5.0×10^{-6}	0.095	6.83×10^{-6}	7.35	29.29
2.5×10^{-6}	0.035	2.52×10^{-6}	7.35	29.58

Ionic strength $\mu=0.064$, Molar absorptivity $\varepsilon = 1.39 \times 10^4$ cm^{-1} mol^{-1} l, Temp. 18.5°C, *C=Initial concn of Co(II) in 50-ml aqueous layer, 3*C=Initial concn. of H_2QS and Z^+ in 50-ml aqueous layer, C_T=Final concn. of the ternary complex in 10-ml $CHCl_3$-extract.