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Spectrophotometric Study on the Extraction of Magnesium(II)-8-Hydroxyquinoline-5-sulfonic Acid Chelate Anion with Zephiramine

Masao Sugawara and Tomihito Kambara

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The ion-pair of magnesium(II)-8-hydroxyquinoline-5-sulfonic acid chelate anion with zephiramine (Z^+Cl^-) was extracted into chloroform. The ternary complex has an absorption maximum at 390 nm in the organic layer. The optimum pH range for the extraction is 10.1—11.4. For the first extract, Beer's law holds for 4.6—20.6 μg of magnesium(II) in 10-ml organic layer, the molar absorptivity being 6.73×10^3 cm^{-1} mol^{-1} l. The composition of the ternary complex is estimated to be $[Mg^{2+}(QS^{2-}Z^+)_2(HQS^-Z^+)]_o$. The extraction equilibrium is given by

$$Mg^{2+} + 3[(HQS^-Z^+)]_o + 2OH^- \rightleftharpoons [Mg^{2+}(QS^{2-}Z^+)_2(HQS^-Z^+)]_o + 2H_2O$$

where QS denotes 8-hydroxyquinoline-5-sulfonic acid and o the organic phase. The equilibrium constant K is given by $\log K = 16.95 \pm 0.13$.

Although magnesium(II) forms with 8-quinolinol a compound $MgOx_2\cdot2H_2O$ slightly soluble in chloroform, Luke and Campbell¹⁾ successfully extracted the compound by using butyl cellosolve as a supplementary solvent to chloroform. Jankowsky and Freiser²⁾ extracted an ion-pair such as tetra-*n*-butylammonium tris-8-quinolinolatomagnesium, $[(C_4H_9)_4N^+Mg(C_9H_6NO)_3^-]$. Extraction of a similar complex was also reported by Umland and Hoffman.³⁾ Fukamachi *et al.*⁴⁾ reported the extraction of magnesium-Eriochrom Black T complex with zephiramine into 1,2-dichloroethane. Nakaya and Nishimura⁵⁾ have reported the extraction of magnesium 8-quinolinolate in the presence of pyridine.

In the present study, magnesium(II)-8-hydroxyquinoline-5-sulfonic acid chelate anion was extracted into chloroform in the presence of zephiramine (tetradecyl-dimethyl-benzyl-ammonium chloride). The composition of the extracted complex as well as fundamental conditions for spectrophotometric determination of magnesium(II) were discussed.

Experimental

Reagent. *Magnesium(II) Standard Solution*: Magnesium sulfate (Wako Chemicals Co.) was dissolved in deionized water. Standardization of the solution was carried out by EDTA-titration using Eriochrom Black T as an indicator. It was found that 228.8 μg of magnesium(II) was contained per milliliter. The solution was diluted as required.

8-Hydroxyquinoline-5-sulfonic Acid Solution (H_2QS): 1.00×10^{-3} M solution was prepared by dissolving H_2QS (Wako Chemicals Co.) in water.

Zephiramine Solution (Z^+Cl^-): 5.00×10^{-3} M solution was prepared by dissolving Dotite zephiramine in water.

Ammonia Buffer Solution, pH 10.0—12.3: 0.1 M stock solutions of ammonium chloride, ammonia and sodium hydroxide were mixed in appropriate proportions.

Borate Buffer Solution, pH 9.2—10.1: Stock solution of 0.05 M borax was suitably mixed with 0.1 M sodium hydroxide.

Chloroform and other reagents were all of analytical reagent. Resin-deionized water was used.

Apparatus. All the measurements were carried out with the same apparatus as that described previously.⁶⁾

Procedure. A definite volume of magnesium(II) standard solution (11.4 μg) was mixed with 15 ml of the H_2QS solution and 5 ml of the zephiramine solution in a 100-ml separatory funnel. pH adjustment was carried out

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1) C. L. Luke and M. E. Campbell, *Anal. Chem.*, **26**, 1778 (1954).

2) S. J. Jankowsky and H. Freiser, *ibid.*, **33**, 776 (1961).

3) F. Umland and W. Hoffmann, *Anal. Chim. Acta*, **17**, 234 (1957).

4) K. Fukamachi, H. Kohara, and N. Ishibashi, *Bunseki Kagaku*, **19**, 1529 (1970).

5) S. Nakaya and M. Nishimura, *ibid.*, **22**, 733 (1973).

6) T. Kambara and M. Sugawara, This Bulletin, **46**, 500 (1973).

with 10 ml of the ammonia buffer solution and then filled up to 50 ml with water. The mixture was shaken for 5 min with 10 ml of chloroform and left for 10 min for the phases to separate. The organic phase was drained into a beaker containing anhydrous Na_2SO_4 and subjected to optical measurement. The absorbance of the extract was measured against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. Absorption spectra of the ternary complex in aqueous and organic phases are shown in Figs. 1 and 2, respectively. The ternary complex has an absorption maximum at 400 nm in the aqueous phase and 390 nm in the organic phase. Color of magnesium(II)–H_2QS complex was not developed at the magnesium(II) concentration used.

Effect of pH. The aqueous solution was adjusted to various pH values with the ammonia buffer solution and the extraction was carried out by the above procedure. The optimum pH range for the extraction was found to be 10.1—11.4. The chloroform extract was stable for at least 30 min. At higher pH, the color of the extract changed with a gradual increase in absorbance. Use of borate buffer solution is not desirable since the absorbance of the reagent blank is very high.

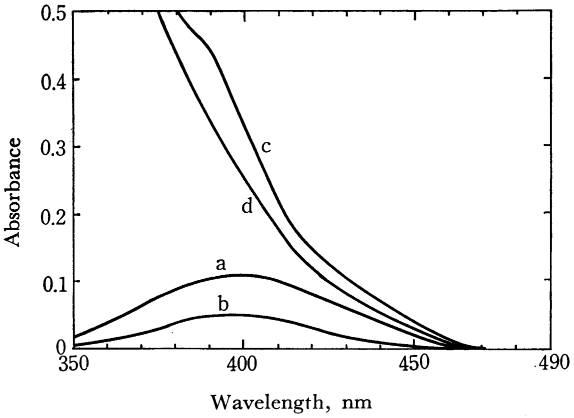

Fig. 1. Absorption spectra of Mg(II)-QS-Z complex in the aqueous solution.
Curve (a): $[\mathrm{Mg(II)}]_w = 1.8\times10^{-5}$ M, (b): 0.94×10^{-5} M; $[\mathrm{QS}]_w = 3.0\times10^{-4}$ M, $[\mathrm{Z}]_w = 5.0\times10^{-4}$ M, pH 10.3,
Curve (a), (b): *vs.* reagent blank, (c): *vs.* water, (d): reagent blank *vs.* water.

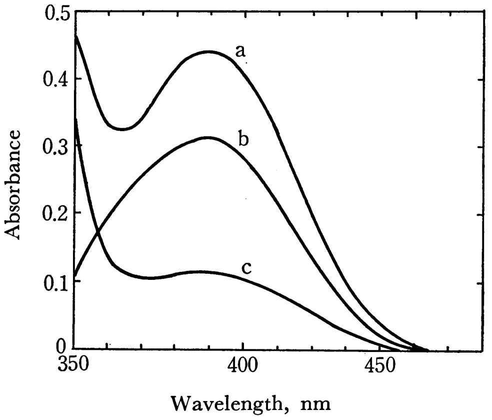

Fig. 2. Absorption spectra of Mg(II)-QS-Z complex in the organic phase after extraction.
Volume of the aqueous phase $V_w = 50$ ml, Volume of the organic phase $V_o = 10$ ml, $[\mathrm{Mg(II)}]_w = 0.94\times10^{-5}$ M, $[\mathrm{QS}]_w = 3.0\times10^{-4}$ M, $[\mathrm{Z}]_w = 5.0\times10^{-4}$ M, pH 10.3,
Curve (a): *vs.* $CHCl_3$, (b): *vs.* reagent blank, (c): reagent blank *vs.* $CHCl_3$.

Effect of H_2QS and Zephiramine Concentration. Varying amounts of reagents were added to the aqueous solution buffered to pH 10.6 and the solution was shaken with chloroform as above. The constant and maximum absorbance of the extract was obtained with a concentration ratio higher than 10-fold of H_2QS and 20-fold of zephiramine to magnesium(II).

Effect of Shaking Time. Shaking time was varied from 2 min to 15 min. The absorbance of the extract was found to decrease when shaking was continued for longer than 10 min. 5 minutes were found to be the desired time for each case.

Extractability and Molar Absorptivity. 25 ml of aqueous solution containing 11.4 μg of magnesium(II) and the reagents of appropriate concentrations was shaken with 10 ml of chloroform. Extraction was repeated with 5 ml of chloroform for the remaining aqueous phase after the separation of the extract. Extractability of magnesium(II) was calculated from absorbances of the extracts. It was found that 98.7% of magnesium(II) was extracted in a single extraction. Molar absorptivity of the ternary complex was 6.73×10^3 $\mathrm{cm^{-1}\,mol^{-1}\,l}$, which is higher than the value obtained by Luke and Campbell's method[1] (5600), or that by Nakaya and Nishimura's method(4420),[5] but lower than that by Jankowsky and Freiser's method (7080).[2]

Calibration Curve. Varying amounts of magnesium(II) were extracted. It was found that Beer's law holds for the first extract, 4.6—20.6 μg of magnesium(II), Sandell's sensitivity for the absorbance of 0.001 being 0.0036 $\mu\mathrm{g\,cm^{-2}}$.

Interference by Calcium Ion. Various amounts of calcium(II) were added to the aqueous solution containing magnesium(II) and the solution was treated by the above. The results are given in Table 1. When the amount of calcium(II) became about 5-fold of magnesium(II), a larger error was observed.

Composition of the Ternary Complex. The continuous variation method for three-component system[6] was used to determine the composition of the ternary complex. Maximum absorbance of the extract was obtained at the mole ratio of Mg(II) : H_2QS : zephiramine = 1 : 3 : 3 (Fig. 3). The composition of the ternary complex was therefore estimated to be $[\mathrm{Mg^{2+}}\text{-}(\mathrm{QS^{2-}\text{-}Z^+})_2(\mathrm{HQS^-\text{-}Z^+})]_o$.

Equilibrium Constant. The continuous variation method applied to the system of H_2QS-zephiramine indicates that an ion-pair of $[\mathrm{HQS^-Z^+}]_o$ was extracted from the ammonia buffer solution (pH 10.2). Thus extraction equilibrium of magnesium(II) is given by

$$\mathrm{Mg^{2+}} + 3\,[(\mathrm{HQS^-Z^+})]_o + 2\,\mathrm{OH^-} \rightleftharpoons [\mathrm{Mg^{2+}(QS^{2-}\text{-}Z^+)_2(HQS^-Z^+)}]_o + 2\,\mathrm{H_2O} \qquad (1)$$

A 50-ml portion of aqueous solution, in which the initial concentrations of magnesium(II), H_2QS and

TABLE 1. DETERMINATION OF MAGNESIUM(II) IN THE PRESENCE OF CALCIUM(II)[a)]

Magnesium(II) taken (μg)	Calcium(II)[b)] added (μg)	Magnesium(II) found (μg)	Recovery (%)	Relative standard deviation (%)	Comparison[c)] of means
11.4	none	11.6	101.8	2.2	
	29.5	11.4	100	0.88	A
	59.0	10.5	92.1	4.8	B
6.87	none	6.67	97.0	10	A
	7.40	7.10	103.3	5.9	A
	14.8	7.20	104.8	8.8	A

a) Each result is the average of three separate analyses. b) Added as nitrate. c) A: No significant difference. B: A significant difference. Significant level: $\alpha=0.05$.

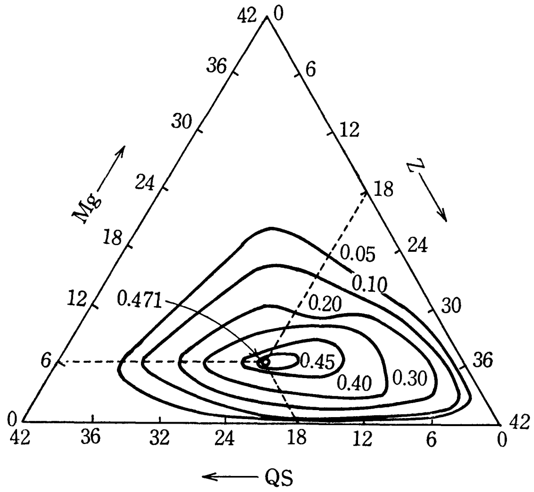

Fig. 3. Continuous variation method applied to the system of Mg(II)-QS-Z complex in the organic phase.
$V_w=50$ ml, $V_o=10$ ml, pH 10.4, $[\text{Mg(II)}]_w+[\text{QS}]_w+[\text{Z}]_w=4.2\times10^{-4}$ M, 390 nm *vs.* reagent blank,
Numerals show the absorbance of organic phase.

zephiramine are $*C$ and $3*C$, respectively, was equilibrated with 10 ml of chloroform. The absorbance of the extract was measured against the reagent blank. Concentration of the ternary complex in the organic phase was calculated from the molar absorptivity. The equilibrium constant of Eq. (1) is given by

$$K=\frac{C_T}{\left[*C-\frac{10}{50}C_T\right]\left[\frac{50}{10}\times3*C-3C_T\right]_o^3\left[\text{OH}^-\right]^2} \quad (2)$$

The results obtained with various concentrations of $*C$ are given in Table 2. The logarithm of the equilibrium constant is $\log K=16.95\pm0.13$.

TABLE 2. EQUILIBRIUM CONSTANT[a)] FOR THE EXTRACTION OF Mg(II)-QS-Z COMPLEX SHOWN BY Eqs. (1)—(2)

$*C$[b)] (M)	Absorbance	C_T[c)] (M)	pH	$\log K$
3.0×10^{-5}	0.065	9.66×10^{-6}	10.4	16.95
6.0×10^{-5}	0.461	6.85×10^{-5}	10.4	17.00
9.0×10^{-5}	0.908	1.35×10^{-4}	10.3	16.90

a) Ionic Strength $\mu=0.03$, Temp. 21.0 °C, Molar Absorptivity $\varepsilon=6.73\times10^3$ cm^{-1} mol^{-1} l. b) Initial concn. of Mg^{2+} in 50-ml aqueous layer, $3*C$=Initial concn. of H_2QS and zephiramine in 50-ml aqueous layer. c) Final concn. of Mg(II)-QS-Z complex in 10-ml chloroform extract.