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Solvent Extraction of Copper(II) with 2-(*o*-Hydroxyphenyl)benzothiazole

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Synopsis. Equilibrium and kinetic aspects of the solvent extraction of Cu(II) with 2-(*o*-hydroxyphenyl)benzothiazole have been carried out using a water–chloroform system. The complex extracted into chloroform was greenish-brown in color and the absorbance at 490.0 nm obeyed Beer's law up to 2×10^{-4} mol/dm^3. The complex was 1:2 (Cu^{2+}:ligand) type and the over-all stability constant, β_2, was 1.3×10^{17} at an ionic strength of 0.3. The extraction constant, K_{ex}, was 2.5×10^{-8}. The extraction kinetics were first order with Cu(II) ions and the reagent anions. The rate constant for the reaction was found to be 5.0×10^{9} mol^{-1} min^{-1}.

Solvent extraction (liquid-liquid extraction) of metal chelate complexes has been used as a separation method for a long time. For extraction of metal ions, it is preferable that the chelating reagent used has a high distribution coefficient (K_{DR}) and pH dependence in the system chosen. Thus, dithizone,[1] 8-quinolinol, cupferron and others have been used widely.[2] In this study, extraction of copper(II) with 2-(*o*-hydroxyphenyl)benzothiazole was investigated. It could have been expected that this reagent would be effective for extraction of certain metal ions because of its high molecular weight and low solubility in water. The reagent forms complex compounds with certain metal ions such as Co(II), Pb(II), and Ni(II).[3] However, there is no report of solvent extraction being attempted with this reagent. On the other hand, its luminescence properties have been studied.[4] In this paper, equilibrium and kinetic studies with this reagent of copper(II) in a water–chloroform system are reported.

Experimental

Reagents. 2-(*o*-hydroxyphenyl)benzothiazole(HPBT) was obtained from INC Pharmaceuticals Inc. All reagents for this study were of reagent grade from Wako Chemical Co. Ltd.

Instrumentation. The atomic absorption spectra were obtained using a Nippon Jarrel Ash AA-1 Mark-II Atomic Absorption Spectrophotometer by the use of air and acetylene flame. The electronic spectra were obtained with a Shimazu UV-240 Spectrophotometer.

All equilibrium extraction were performed by agitating the samples in 25 dm^3 vials for 30 min (120 strokes/min) at 25±1 °C. After agitation, the solutions were allowed to stand for 10 min before further operations were carried out.†

The kinetic study was carried out in the same manner as the equilibrium investigation, and only the agitating time was changed.

Measurement of Reagent Distribution Constant (K_{DR}). Equal volumes (6 dm^3) of 0.1 mol/dm^3 solution of HPBT in chloroform and the appropriate buffer solution were shaken and the aqueous phase was pipetted into a glass tube and centrifuged. The pH was adjusted to the first measured pH. Then 4.5 dm^3 each of the aqueous phase and chloroform were shaken together. The absorbance of the organic phase at 334.7 nm was measured. The distribution ratio D was obtained by the $D=(\varepsilon\ C_o-A_f)/A_f$, where ε is the molar absorptivity, C_o is original concentration of HPBT in chloroform and A_f is final absorbance of the chloroform layer.

Distribution Measurement of Copper(II). A 5-dm^3 chloroform solution of HPBT (0.01—0.03 mol/dm^3) and an equal volume of a buffer solution (pH, 1—13) containing Cu(II) ion*1 of 2×10^{-4} mol/dm^3 were agitated. The copper content in the chloroform layer was determined by atomic absorption spectra using the 324.8-nm line.

The absorption spectra of the chloroform layer were determined over the range 350—700 nm. At 490.0 nm the absorbance obeyed Beer's law up to 2×10^{-4} mol/dm^3 of Cu(II). Consequently, the determination of copper extracted into chloroform was carried out by the spectrophotometric method.

The extractability (E%) and distribution ratio (D) are obtained by the equations $E\%=A_2/A_1\times100$ and $D=E/(100-E)$, where A_1, is the copper concentration in the initial aqueous phase and A_2 is the copper concentration in the chloroform at extraction equilibrium.

Measurement of Distribution Coefficient of Copper Complex (K_{DC}). 5 dm^3 each of 2×10^{-1} mol/dm^3 of HPBT solution in chloroform and 2×10^{-3} mol/dm^3 of copper ion*2 in buffer solution (pH=9.0) were agitated. Then 4.5 dm^3 each of the aqueous layer and chloroform were shaken and the absorbance of the chloroform layer was measured at 490.0 nm. K_{DC} can be obtained as the equation $K_{DC}=A_1/A_2$, where A_1 and A_2 are absorbance of the chloroform layers first and second extracted, respectively.

Results and Discussion

The theoretical basis for the determination of the several constants will not be discussed here in detail. They are not special and a number of references are available.[5–7]

Distribution of Reagent. Experimental results were shown in Fig. 1. The constants for HPBT are tabulated in Table 1.

Extraction of Copper. Extractability of copper changes according to pH as was showm in Fig. 2. The plots of log D against pH (fixed concentration of HPBT) or log [HPBT] (fixed pH) showed linear relations and their slopes were all 2. The results indicate the extracted complex has 1:2 (Cu^{2+}:HPBT) composition.[8] The results for the complex were summarized in Table 2. The over-all stability constant (β_2) is smaller than that of the 8-quinolinol complex (23.4)[9] although the molecular weight of HPBT is larger and pK_{a2} is higher as compared with the respective values for 8-quinolinol. It can be presumed that HPBT forms a six-membered chelate ring with the metal ion but 8-quinolinol forms a five-membered chelate ring. Free rotation of the hydroxyphenyl group and the bonding distance with copper(II) may influence the result.

Kinetic of Extraction of Copper(II) Ion. The reaction with the metal ion was taken to obey a first order reaction by analogy with other work.[10] The

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†The condition was investigated previously.

*1, *2, Copper (II) acetate was used. The results when copper (II) nitrate was used did not change.

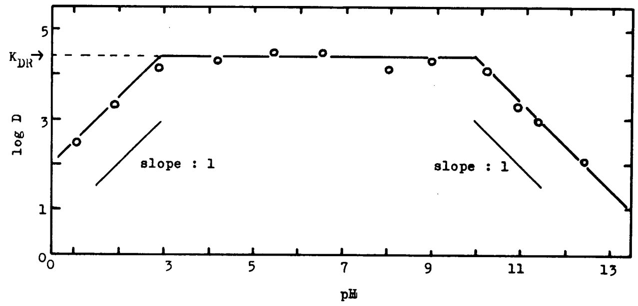

Fig. 1. Distribution ratio change of HPBT with pH in water-chloroform system.

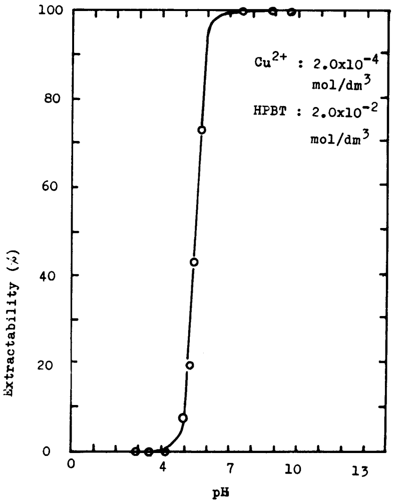

Fig. 2. Extractability change of Cu^{2+} with HPBT with pH.

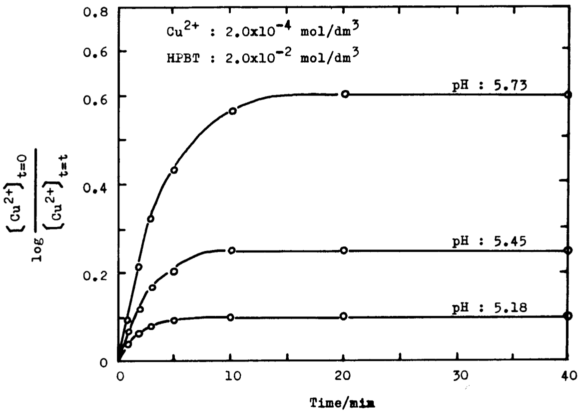

Fig. 3. Relationship between $\log[Cu^{2+}]_{t=0}/[Cu^{2+}]_{t=t}$ and extraction time.

reaction rate should be given by

$$-d[Cu^{2+}]/dt=k[Cu^{2+}][PBT^-] \qquad (1)$$

for the slowest reaction $Cu^{2+}+PBT^- \rightarrow [Cu\cdot PBT]^+$. For this reaction, the rate constant, k, is presented. An equation

$$\log(\log[Cu^{2+}]_{t=0}/[Cu^{2+}]_{t=t}) = \log(kK_{a2}/2.303K_{DR}) + \log[HPBT]_o + pH + \log t$$

can be obtained by substituting $K_{a2}=[H^+][PBT^-]/[HPBT]$ and $K_{DR}=[HPBT]_{org}/[HPBT]_w$ into the Eq. 1 and integration. The plots of $\log(\log[Cu^{2+}]_{t=0}/[Cu^{2+}]_{t=t})$ *vs.* pH and $\log[HPBT]_0$ showed linear relations with all slopes equal to unity, indicating that the rate-determining step was controlled by the formation of the 1 : 1 complex. The initial slopes were changed in the plots of $\log[Cu^{2+}]_{t=0}/[Cu^{2+}]_{t=t}$ *vs.* time as were shown in Fig. 3. The kinetic data are shown in Table 3. From this the rate constant, k, can be calculated by the relation $k=k'\times K_{DR}/K_{a2}$, where k'=slope×2.303[H⁺]/ [HPBT]₀.

Table 1. Distribution and dissociation constants of HPBT

$\log K_{DR}$*1	$pH_{1/2}$*2	pK_{a1}	$pH_{1/2}$*2	pK_{a2}
4.4	−1.6	2.8	14.5	10.1

*1, $K_{DR}=[HPBT]_o/[HPBT]_w$, *2, At these points, $\log D=0$

Table 2. Extraction and stability constants of Cu(II) complex

$pH_{1/2}$*1	K_{DC}	K_{ex}	β_2
5.5	2.0×10^4	2.5×10^{-8}	1.3×10^{17}

*1, 50% of Cu^{2+} is extracted into chloroform from water.

Table 3. Kinetic data for extraction of Cu(II)

$[HPBT]_0$	$[H^+]$	slope	k'
2.0×10^{-2}	6.61×10^{-6}	2.07×10^{-2}	1.58×10^{-5}
2.0×10^{-2}	3.55×10^{-6}	3.91×10^{-2}	1.60×10^{-5}
2.0×10^{-2}	1.86×10^{-6}	10.6×10^{-2}	2.27×10^{-5}
1.4×10^{-2}	6.61×10^{-6}	1.19×10^{-2}	1.29×10^{-5}
1.4×10^{-2}	3.55×10^{-6}	3.15×10^{-2}	1.84×10^{-5}
1.4×10^{-2}	1.86×10^{-6}	5.05×10^{-2}	1.55×10^{-5}
1.0×10^{-2}	6.61×10^{-6}	0.90×10^{-2}	1.37×10^{-5}
1.0×10^{-2}	3.55×10^{-6}	1.70×10^{-2}	1.39×10^{-5}
1.0×10^{-2}	1.86×10^{-6}	3.11×10^{-2}	1.33×10^{-5}
			Av. 1.58×10^{-5}

The value of k thus obtained was 5.0×10^9 mol^{-1} min^{-1}. The value is relatively large compared with the case of the extraction of Co^{2+} and Ni^{2+} with dithizone. It is assumed that this is due to the Jahn-Teller effect. Namely, water molecules on the z axis are liberated easily.[7] For Co^{2+} extraction with HPBT, we obtained $k=4.2\times10^5$ mol^{-1} min^{-1}.

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