Highly Selective Copper(II) Extraction with Oligoethylene Glycol Bis(hydrazone)s as Several Compositional Complexes

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High Cu^{2+} ion selectivity in the solvent extraction was spectrophotometrically exhibited by using the non-cyclic polyether derivatives bearing a 5-nitro-2-pyridyl-hydrazone at each end of the bridging chain. The species of Cu^{2+} complexes extracted were changed with the variation of additional alkali metal salts.

Hydrazone derivatives with several heterocyclic groups have been so far widely investigated as organic reagents for colorimetric determination of heavy metal ions.[1,2] It is known that these hydrazones extract effectively some kind of divalent metal ions as 2:1 complex (ligand:metal ion) from aqueous phase into organic phase.[3] It occurred to us that a bis(hydrazone) derivative bearing two hydrazone groups in a molecule will be possible to form stable complex with metal ion selectively. On the other hand, a number of cyclic and non-cyclic oligoethylene glycols, so-called crown ether and podand and so on, have been synthesized and investigated as ionophores for complexation with particular alkali metal ions. From the points in enhancement of the extractability and in increase of the ion selectivity for certain heavy metal ions, it is very interesting to work up the cooperative extraction system[4] between divalent heavy metal ion with the hydrazone groups and alkali metal ion with the bridging ether chain moiety.

In this paper we will describe extremely high Cu^{2+} ion selectivity of oligoethylene glycol bis(hydrazone)s, 1-4, in the solvent extraction,

1, 2, 3, 4   5
n= 1, 2, 3, 4
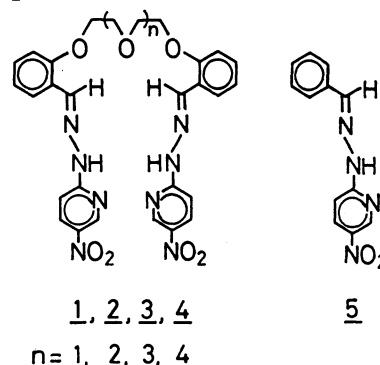
their pH-dependence of extraction
behavior and cooperative effect of
alkali metal ions on the Cu^{2+} extract-
ability.

    The reaction of 5-nitro-2-
pyridylhydrazine with appropriate α,ω-
bis(2-formylphenoxy)oligoethylene
glycol (ethanol, acetic acid, reflux)
afforded the corresponding hydrazones,
1, 2, 3, and 4, which were purified
with recrystallization from acetone.
The benzaldehyde hydrazone 5 was also
synthesized by the similar procedure
for a comparison.   These compounds
were identified by the elemental
analysis, infrared and mass spectro-
scopic methods.   Their proton-
dissociation constants are shown in
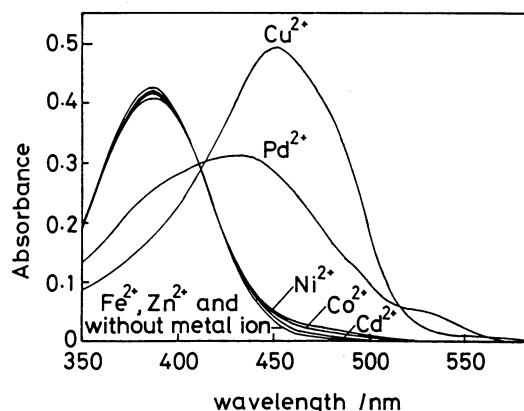Table 1.   The extraction was carried

Fig. 1. Spectral changes in
organic phase on the extraction of
divalent heavy metal ions with 1.
Organic phase: [1] = 1.1 x 10^{-5}
mol dm^{-3} in 1,2-dichloroethane;
Aqueous phase: [metal ion] = 1.0 x
10^{-3} mol dm^{-3} at pH 6.2 except
for the case of Pd^{2+} at pH2.2.

Table 1. Proton-dissociation constants[a] of hydrazones and their Cu^{2+}
extraction equilibrium constants[b] in the presence of Li^+, Na^+, or K^+

| Ligand | pK_{a1} | pK_{a2} | Cu^{2+} extraction equilibrium constant (log K_{ex}) for each complex (ligand:Cu^{2+})[c] | | | | | | | | |
| | | | in the presence of Li^+ | | | in the presence of Na^+ | | | in the presence of K^+ | | |
			2:1	1:1	2:2	2:1	1:1	2:2	2:1	1:1	2:2
1	10.4	13.5	-0.19	--	-7.91	-0.20	--	-7.91	-0.20	--	-7.91
2	10.5	13.5	0.39	--	-7.89	0.40	--	-7.90	0.40	--	-7.90
3	11.3	13.6	0.57	-7.05	-8.27	0.74	-6.68	-8.16	0.97	-6.43	--
4	12.4	13.6	-0.99	--	-9.30	-0.24	-7.00	-9.01	2.01	-5.76	--
5	12.8										

a) 1,4-dioxane - H_2O (72/28 vol%), μ = 0.2 (($CH_3)_4NCl$)   b) organic phase: [ligand] =
1.0 x 10^{-5} mol dm^{-3}; aqueous phase: [Cu^{2+}] = 2.0 x 10^{-4} mol dm^{-3}, [alkali metal ion]
= 0.1 mol dm^{-3}, pH 2.5 - 6.5.   c) 2:1, 1:1, and 2:2 complexes correspond to $Cu(HL)_2$,
CuL, and Cu_2L_2, respectively.

out at 25 °C by varying proton concentration (pH) at an appropriate metal concentration in the aqueous phase and keeping the hydrazone concentration constant in 1,2-dichloroethane.   The extraction behavior was evaluated by the spectrophotometric method for the organic phase.

Fig. 1 shows the extraction behavior of diethylene glycol bis-(hydrazone) $\underline{1}$, exhibiting high Cu^{2+} selectivity over Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, and Cd^{2+} at pH 6.2, except for Pd^{2+} extracted at pH 2.2.   In addition, extractions of alkali metal and alkaline earth metal ions were not observed under the conditions at all.   The extraction behavior was also supported by the back-extraction experiment of the extracts with acidic aqueous solution, in which metal ion concentrations were detected by atomic absorption spectroscopy.   Similar cation selectivities were seen in the cases using the other analogues.   The extractabilities of the hydrazones for Cu^{2+} were decreased in the order $\underline{1}$ > $\underline{2}$ > $\underline{3}$ > $\underline{4}$ >> $\underline{5}$ above pH 5.5, and the monohydrazone $\underline{5}$ hardly extracted Cu^{2+} (Fig. 2). This result shows that bis(hydrazone)s bridged with oligoethylene glycol unit play a highly effective extractant of Cu^{2+}, and that the shorter the bridging unit the more extractable.

The apparent molar absorptivity vs. pH curve (Fig.2) for Cu^{2+} complexes of $\underline{2}$ shows three inflections at pH about 4.0, 4.9, and 5.8. The result of the continuous variation method performed at pH 4.9 and 6.9 for $\underline{2}$ demonstrated that the ligand formed Cu^{2+} complexes with 2:1 (ligand:Cu^{2+}) and 1:1 compositional ratios.   The compositions of the Cu^{2+} complexes were investigated in detail by evaluating the absorbance values obtained on the solvent extraction with LiCl for adjusting ionic strength (Table 1).[5]   When formation of 2:1 and 1:1 complexes of $\underline{2}$ with Cu^{2+} are assumed, the calculated values are systematically deviated from the measured ones.   Therefore, by considering formation of 2:1, 1:1,
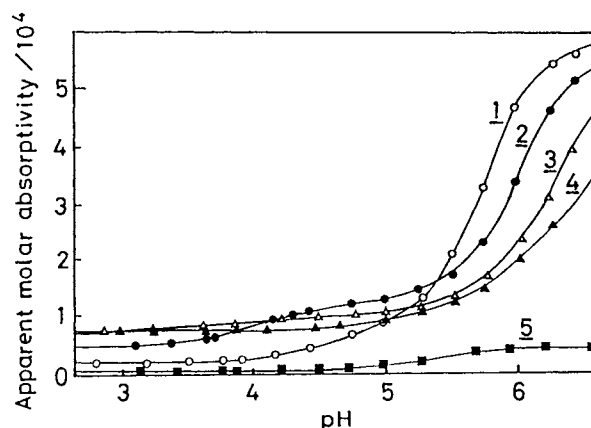

Fig. 2. Plots of apparent molar absorptivity of Cu^{2+} complexes extracted at 450 nm in organic phase versus pH value in aqueous phase. Organic phase: [hydrazone unit] = 2.0 x 10^{-5} mol dm^{-3} in 1,2-dichloro-ethane. Aqueous phase: [Cu^{2+}] = 2.0 x 10^{-4} mol dm^{-3}, μ = 0.1 (LiCl).

and 2:2 complexes, an excellent agreement between experimental and calcu-
lated values was obtained, although no 1:1 complex was exhibited for 2.
Similar results were observed in the cases of the analogues except for 3.
It is probably because the bridging oligoethylene glycol unit would not
be flexible enough to form a pseudo-cyclic intramolecular 1:1 complex,
which is formed by two hydrazones of both ends of the bridging chain and a
Cu^{2+}.

Interestingly enough, addition of NaCl or KCl, instead of LiCl, to
the aqueous solution containing Cu^{2+} increased the formation of intramole-
cular 1:1 complexes of Cu^{2+} with 3 and 4 very effectively (Table 1).   In
practice, when sodium or potassium picrates which are more lipophilic than
the chlorides were used for adjusting the ionic strength, the formation of
1:1 complex slightly further increased and the extractions of their
picrates into the organic phase were observed.   It is presumed that Na^+
and K^+ might interact with the ethereal oxygens of ethylene glycol unit as
a template to make a pseudo-cyclic conformation like a crown ether[6] and
therefore two hydrazone groups on either end of the ligand could be closed
each other more easily when the ligand coordinates to Cu^{2+} to form 1:1
complex.   Further details of the investigation are in progress.

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4) T. Nabeshima, T. Inaba, T. Sagae, and N. Furukawa, *Tetrahedron Lett.*,
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5) The extraction equilibrium constants, which are shown in Table 1, were
   calculated according to the following equations by a non-linear least-
   square method from the absorbance at the wavelength of maximal absorp-
   tion of the organic phase: $K^{ex}_{M(HL)2} = [H^+]^2[M(HL)_2]_o/([M^{2+}][H_2L]_o^2)$; K^{ex}_{ML}
   $= [H^+]^2[ML]_o/([M^{2+}][H_2L]_o)$; $K^{ex}_{M2L2} = [H^+]^4[M_2L_2]_o/([M^{2+}]^2[H_2L]_o^2)$, where
   H_2L, $M(HL)_2$, ML, and M_2L_2 mean neutral ligand, 2:1, 1:1, and 2:2 com-
   plexes of the ligand with Cu^{2+}, respectively, and subscript "o" and the
   lack of subscript denote an organic and an aqueous phase, respectively.
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