# Liquid–Liquid Distribution Behavior of Ion Association Complexes of Dihalogenocuprate(I) Anions with Azo-Dye Cations as Counter Ions

**Koichi YAMAMOTO**† and **Shoji MOTOMIZU**

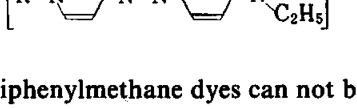
*Department of Chemistry, Faculty of Science, Okayama University, Okayama 700, Japan*

The solvent extraction of ion association complexes of dihalogenocuprate(I) ions $CuX_2^-$($X^-$=chloride, bromide and iodide ions), with 4-(4-diethylaminophenylazo)-*N*-alkylpyridinium cations (azo-dye cations) is described: the alkyl groups of the azo-dye cations were methyl, ethyl and propyl groups. The extraction constants ($K_{ex}$) for the ion association complexes of $CuX_2^-$ and $X^-$ with these three azo-dye cations between an aqueous phase and several organic phases (chloroform, chlorobenzene, benzene and toluene) were determined. The extractabilities of $CuX_2^-$ and $X^-$ were in the orders $CuCl_2^- < CuBr_2^- < CuI_2^-$, and $Cl^- < Br^- < I^-$, respectively: the differences in log $K_{ex}$ between two successive ions averaged about 1.2 and 1.3 for $CuX_2^-$ and about 1.2 and 1.9 for $X^-$. In all of the ion association complexes examined, the order of the values of the extraction constants was chloroform>chlorobenzene>benzene>toluene. The difference in the value of log $K_{ex}$ between chloroform and chlorobenzene for $CuX_2^-$ was much smaller than that for $X^-$, while between other solvents the differences in log $K_{ex}$ values for $CuX_2^-$ and $X^-$ were almost the same. From the extraction constants obtained, some possible extraction systems for a spectrophotometry for copper are predicted: they include one using chlorobenzene, the methyl derivative of the azo-dye, and iodide ion and one using chlorobenzene, the propyl derivative of the azo-dye and bromide ion.

**Keywords** Solvent extraction, copper, dihalogenocuprate(I)-azo dye ion association complex, 4-(4-diethylaminophenylazo)-*N*-alkylpyridinium cation

Dichlorocuprate(I) anion has been used for the selective separation of copper.[1,2] Several cationic dyes have frequently used in solvent extraction–spectrophotometric determinations of metals as complex anions and non-metallic anions.[3] Recently the authors reported the solvent extraction–spectrophotometric method[4] for copper using Ethyl Violet as a counter ion of dichlorocuprate(I) anion: the method was applied to the determination of trace amounts of copper in steel, stainless steel and aluminum alloy samples.[5]

In this work, the authors report the extraction behavior of ion association complexes of dihalogenocuprate(I) and halide ions with 4-(4-diethylaminophenylazo)-*N*-alkylpyridinium cations as follows:



$R=CH_3$(MEP)
$C_2H_5$(EEP)
$C_3H_7$(PEP)

Triphenylmethane dyes can not be used for the study of the extraction equilibrium, because these dyes fade during the extraction procdure.

## Experimental

### *Apparatus*

A Shimadzu UV 300 recording spectrophotometer and a Hitachi Perkin-Elmer 139 spectrophotometer were used for recording spectra and absorbance measurements in quartz cells of 10-mm path length. A Hitachi–Horiba Model F-5 pH meter was used for pH measurements. Extractions were carried out by horizontal shaking with a Taiyo Model SR-I reciproshaker.

### *Reagents*

*4-(4-Diethylaminophenylazo)-N-alkylpyridinium salts (cationic azo dyes).* Cationic azo dyes used were the ones synthesized and used in the previous work.[6] 4-(4-Diethylaminophenylazo)-*N*-alkylpyridinium iodides were dissolved in water, and the solutions were passed through an anion-exchange resin (Dowex SBR-P, $Cl^-$ form) in a glass column (20 cm long and 2 cm

---

† On study leave from Department of Industrial Chemistry, Yonago National College of Technology, Yonago, Tottori 683, Japan

diameter). The eluate was transferred to a suitable volumetric flask and diluted to the mark with water.

*Standard copper(II) solution, $1\times10^{-2}$ M.* Prepared by dissolving 1.25 g of copper(II) sulfate pentahydrate in 0.05 M sulfuric acid solution to give a 500 ml solution. The concentration was determined by EDTA titration using 1-(2-pyridylazo)-2-naphthol (PAN) as indicator. Working solutions were prepared by accurate dilution of the standard solution.

*Reducing agent, $1\times10^{-2}$ M.* Prepared by dissolving 0.176 g of ascorbic acid in 100 ml of distilled water daily.

*Buffer solution.* This was prepared by mixing 0.5 M acetic acid and 0.5 M sodium acetate solutions, the pH being adjusted to 6.0 with a pH meter.

*Halide ion solution.* Sodium halides were dissolved in distilled water. These solutions were used for the formation of copper(I)-halogeno complexes. Fresh sodium iodide was prepared as needed.

*Extracting solvents.* Commercially available toluene, benzene, chlorobenzene and chloroform were used after washing with distilled water.

All reagents were of analytical-reagent grade and were used without further purification.

*Determination of the extraction constants*

An extraction system in which a monovalent cation ($C^+$) reacts with a monovalent anion ($A^-$) to form only one kind of ion association complex ($C^+\cdot A^-$) in the aqueous phase, and the extracted ion association complex does not dissociate or aggregate, involves the following equilibrium:

$$C^+ + A^- \rightleftharpoons C^+\cdot A^- \rightleftharpoons (C^+\cdot A^-)_{org} \quad (1)$$

where the subscript org refers to the organic phase and the aqueous phase is unmarked.

The extraction constant $K_{ex}$, is described by the following equation:

$$K_{ex} = [C^+\cdot A^-]_{org}/[C^+][A^-]. \quad (2)$$

*Procedure.* One milliliter of $1\times10^{-4}$ M copper(II) solution was transferred to a 25-ml stoppered test tube. To it 0.5 ml of $1\times10^{-2}$ M ascorbic acid solution, an appropriate amount of sodium halide solution, 1 ml of 0.5 M acetate buffer solution and an appropriate amount of the azo dye solution were added. The solution was diluted to 10 ml with distilled water or with sodium sulfate solution. The ionic strength of the aqueous solution was adjusted with sodium sulfate. The aqueous solution was shaken with 5 ml of an extracting solvent for 30 min. After the phase separation, the absorbance of the organic phase was measured at the wavelength of absorption maximum against an extracting solvent as reference. The concentration of the ion association complex in the organic phase was calculated from Eq. (3),

$$A_{(o)} = \varepsilon_{CuX_2^-(o)} \times C_{CuX_2^-(o)} + \varepsilon_{X^-(o)} \times C_{X^-(o)} \quad (3)$$

where $A_{(o)}$ is the absorbance of the organic phase, $\varepsilon_{CuX_2^-(o)}$ and $\varepsilon_{X^-(o)}$ the molar absorptivities of the ion association complexes of $CuX_2^-$ and $X^-$ in the organic phase, respectively, and $C_{CuX_2^-(o)}$ and $C_{X^-(o)}$ the concentrations of the ion association complexes of $CuX_2^-$ and $X^-$ in the organic phase. In the later calculations, the values of the molar absorptivities obtained by using dodecylsulfate as a counter anion of azo-dye cations and by using 1,2-dichloroethane as an extracting solvent of ion associates formed were used instead of $\varepsilon_{CuX_2^-(o)}$ and $\varepsilon_{X^-(o)}$. The value of $C_{X^-(o)}$ can be calculated by using the extraction constant for $X^-$; in most of the extraction systems, the absorbance of the reagent blank of the extraction system is substituted for the values of $\varepsilon_{X^-(o)}\times C_{X^-(o)}$. The concentrations of the dye and of $CuX_2^-$ in the aqueous phase after extraction were determined by substracting the total concentrations of the ion association complexes in the organic phase from the initial concentrations of the dye or the copper(II), respectively.

Procedures for the determination of the extraction constants of halide ions were similar to those for dihalogenocuprate(I) ions, except the addition of the ascorbic acid solution.

All the experiments were carried out in a thermostated room at 25.0±0.1°C.

## Results and Discussion

*Effect of pH*

Cationic dyes may be present in aqueous solutions in two forms: protonated and deprotonated. The dissociation constant of the methyl derivative (MEP), $pK_a$, is 3.69.[7] In the previous work[4], it was found that dichlorocuprate(I) ion formed in the pH range 3.6–5.7. In this work, the extractions were carried out at pH 5.4 with an acetate buffer solution.

*Effect of reducing agent*

The effect of reducing agents on the formation of dichlorocuprate(I) ion was examined with PEP. The results are shown in Fig. 1. By using ascorbic acid, the constant absorbance was obtained at the concentration of chloride ion above 0.10 M, while with hydroxyammonium sulfate, a larger concentration of chloride ion is necessary to complete the dihalogenocuprate complex. In the further experiments, ascorbic acid was used as the reducing agent of copper(II).

The effect of the amount of ascorbic acid on the formation of dichlorocuprate(I) ion was also examined. The volume of $1\times10^{-2}$ M ascorbic acid added was varied from 0.2 to 1.0 ml. The results are shown in Fig. 2. The approximately constant absorbance was obtained at the volume of ascorbic acid solution from 0.4 to 0.7 ml. The decreases in absorbance below 0.4 ml and above 0.7 ml of ascorbic acid solution are caused

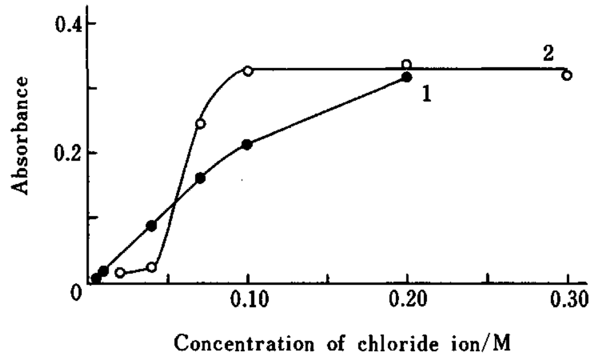


Fig. 1 Effect of reducing agent and chloride ion on the formation of dichlorocuprate(I) ion. $[Cu^{2+}]_{initial}=1\times10^{-5}$ M. $[PEP]_{initial}=2\times10^{-4}$ M. Extracting solvent: chlorobenzene. Curve 1: $1\times10^{-3}$ M hydroxyammonium sulfate, pH 6.2 (acetate buffer); 2: $1\times10^{-3}$ M ascorbic acid, pH 5.4 (acetate buffer). Reference: reagent blank.

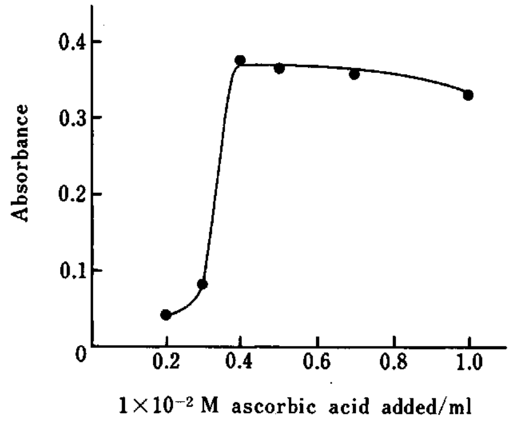


Fig. 2 Effect of amount of ascorbic acid on the formation of dichlorocuprate(I) ion. $[Cu^{2+}]_{initial}=1\times10^{-5}$ M. $[PEP]_{initial}=2\times10^{-4}$ M. $[Cl^-]_{initial}=0.15$ M. Extracting solvent: chlorobenzene. Reference: reagent blank.

by the incomplete reduction of copper(II) to copper(I) and the fading of the azo dye, respectively. Therefore, 0.5 ml of $1\times10^{-2}$ M ascorbic acid was used in the later experiments.

*Effect of amount of halide ion*

The formation of dihalogenocuprate(I) ion can be affected by the concentration of halide ion in the aqueous phase and the extractability of the ion association complex. This effect was examined for each ion association complex by using the different concentrations of halide ion. The results are shown in Fig. 3. The ranges of the concentration of halide ion in which the constant absorbance are obtained are different in the species of dihalogenocuprate(I) ions and azo-dye cations. In the determination of the extraction constants for ion association complexes of $CuX_2^-$ with azo-dye cations, the concentrations of halide ions at which the constant absorbances were obtained were used.

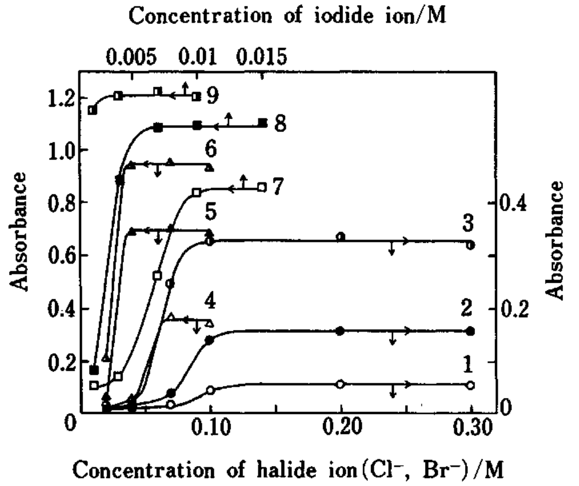


Fig. 3 Effect of amount of halide ion. $[Cu^{2+}]_{initial}=1\times10^{-5}$ M. Extracting solvent: chlorobenzene. Curve 1 (○): $CuCl_2^-$, $[MEP]_{initial}=4\times10^{-4}$ M; 2 (●): $CuCl_2^-$, $[EEP]_{initial}=3\times10^{-4}$ M; 3 (◑): $CuCl_2^-$, $[PEP]_{initial}=2\times10^{-4}$ M; 4 (△): $CuBr_2^-$, $[MEP]_{initial}=2\times10^{-4}$ M; 5 (▲): $CuBr_2^-$, $[EEP]_{initial}=1.5\times10^{-4}$ M; 6 (◭): $CuBr_2^-$, $[PEP]_{initial}=1\times10^{-4}$ M; 7 (□): $CuI_2^-$, $[MEP]_{initial}=5\times10^{-5}$ M; 8 (■): $CuI_2^-$, $[EEP]_{initial}=5\times10^{-5}$ M; 9 (◧): $CuI_2^-$, $[PEP]_{initial}=5\times10^{-5}$ M. Reference: reagent blank.

*Determination of the extraction constants and some considerations of the extractability of ion association complexes*

Toluene, benzene, chlorobenzene and chloroform were used as the extracting solvent. The extraction constants ($K_{ex}$) with three azo-dye cations were determined according to Eq. (2). The results obtained are listed in Table 1.

The differences in $\log K_{ex}$, $\Delta\log K_{ex}$, between halide ions and between dihalogenocuprate(I) complex ions are summarized in Table 2. The order of the extractability of ion association complexes of $X^-$ and $CuX_2^-$ was $I^->Br^->Cl^-$ and $CuI_2^->CuBr_2^->CuCl_2^-$, respectively; the differences in $\log K_{ex}$ between two successive anions averaged 1.93 and 1.20 for $X^-$, and 1.34 and 1.17 for $CuX_2^-$. The differences in $\log K_{ex}$ between halide ions and between dihalogenocuprate(I) ions were almost equal in these extraction systems.

The differences in $\log K_{ex}$ between azo-dye cations are summarized in Table 3. The order of the extractability of the azo-dye cations was PEP>EEP>MEP, and the differences in $\log K_{ex}$ between two successive cationic dyes averaged 0.64 and 0.58, respectively; the differences in $\log K_{ex}$ between azo-dye cations were almost equal even though the extracting solvents and anions as counter ions were changed. In the previous work, the concentration of methylene group to the extraction constant was averaged to 0.59[8]: that is in

Table 1 Extraction constants (log $K_{ex}$) obtained between aqueous and organic phases

| Anions | Dye cations | Extracting solvents[a] | $[X^-]_{initial}$/M | Ionic strength | log $K_{ex}$ |
|---|---|---|---|---|---|
| $I^-$ | PEP | T | 0.015 | 0.10 | −0.75±0.04 |
| $CuI_2^-$ | MEP | T | 0.015 | 0.10 | 2.77±0.02 |
| $CuI_2^-$ | EEP | T | 0.015 | 0.10 | 3.04±0.02 |
| $CuI_2^-$ | PEP | T | 0.015 | 0.10 | 3.82±0.03 |
| $I^-$ | PEP | B | 0.015 | 0.10 | −0.19±0.02 |
| $CuI_2^-$ | MEP | B | 0.015 | 0.10 | 3.07±0.03 |
| $CuI_2^-$ | EEP | B | 0.015 | 0.10 | 3.53±0.03 |
| $CuI_2^-$ | PEP | B | 0.015 | 0.10 | 4.43±0.04 |
| $Br^-$ | MEP | Cl-B | 0.100 | 0.15 | −1.87±0.05 |
| $I^-$ | MEP | Cl-B | 0.015 | 0.10 | 0.09±0.01 |
| $Cl^-$ | EEP | Cl-B | 0.200 | 0.25 | −2.35±0.07 |
| $Br^-$ | EEP | Cl-B | 0.100 | 0.15 | −1.31±0.02 |
| $I^-$ | EEP | Cl-B | 0.010 | 0.10 | 0.85±0.01 |
| $Cl^-$ | PEP | Cl-B | 0.050 | 0.10 | −1.72±0.03 |
| $Br^-$ | PEP | Cl-B | 0.050 | 0.10 | −0.74±0.04 |
| $I^-$ | PEP | Cl-B | 0.005 | 0.10 | 1.47±0.01 |
| $CuCl_2^-$ | MEP | Cl-B | 0.200 | 0.25 | 2.32 |
| $CuBr_2^-$ | MEP | Cl-B | 0.100 | 0.15 | 3.54±0.02 |
| $CuI_2^-$ | MEP | Cl-B | 0.015 | 0.10 | 4.80±0.08 |
| $CuCl_2^-$ | EEP | Cl-B | 0.200 | 0.25 | 2.98±0.01 |
| $CuBr_2^-$ | EEP | Cl-B | 0.070 | 0.15 | 4.08±0.02 |
| $CuI_2^-$ | EEP | Cl-B | 0.010 | 0.10 | 5.49±0.10 |
| $CuCl_2^-$ | PEP | Cl-B | 0.200 | 0.25 | 3.48±0.01 |
| $CuBr_2^-$ | PEP | Cl-B | 0.070 | 0.15 | 4.65±0.01 |
| $Cl^-$ | MEP | CF | | | −0.08[b] |
| $Br^-$ | MEP | CF | | | 1.19[b] |
| $I^-$ | MEP | CF | | | 3.01[b] |
| $Cl^-$ | EEP | CF | | | 0.57[b] |
| $Br^-$ | EEP | CF | | | 1.90[b] |
| $I^-$ | EEP | CF | | | 3.54[b] |
| $Cl^-$ | PEP | CF | | | 1.11[b] |
| $Br^-$ | PEP | CF | | | 2.49[b] |
| $I^-$ | PEP | CF | | | 4.26[b] |
| $CuCl_2^-$ | MEP | CF | 0.100 | 0.15 | 3.24±0.05 |
| $CuBr_2^-$ | MEP | CF | 0.050 | 0.10 | 4.42±0.03 |

a. Solvent: T, toluene; B, benzene; Cl-B, chlorobenzene; CF, chloroform. b. The value of log $K_{ex}$ in ref. 12.

Table 2 Differences in log $K_{ex}$, Δ log $K_{ex}$, between halide ions and between dihalogenocuprate (I) complex ions

| Extracting solvents[a] | Dye cations | Δ log $K_{ex}$ between anions | |
|---|---|---|---|
| | | $I^-$-$Br^-$ | $Br^-$-$Cl^-$ |
| Cl-B | MEP | 1.96 | |
| Cl-B | EEP | 2.16 | 1.04 |
| Cl-B | PEP | 2.21 | 0.98 |
| CF | MEP | 1.82 | 1.27 |
| CF | EEP | 1.64 | 1.33 |
| CF | PEP | 1.77 | 1.38 |
| | ave. | 1.93±0.28 | 1.20±0.20 |
| | | $CuI_2^-$-$CuBr_2^-$ | $CuBr_2^-$-$CuI_2^-$ |
| Cl-B | MEP | 1.26 | 1.22 |
| Cl-B | EEP | 1.41 | 1.10 |
| Cl-B | PEP | | 1.17 |
| CF | MEP | | 1.18 |
| | ave. | 1.34±0.07 | 1.17±0.06 |

a. Solvents: Cl-B, chlorobenzene; CF, chloroform.

Table 3 Differences in log $K_{ex}$, Δ log $K_{ex}$, between azo dye cations

| Extracting solvents[a] | Anions | Δ log $K_{ex}$ | |
|---|---|---|---|
| | | PEP-EEP | EEP-MEP |
| T | $CuI_2^-$ | 0.78 | 0.27 |
| B | $CuI_2^-$ | 0.90 | 0.46 |
| Cl-B | $Cl^-$ | 0.63 | |
| Cl-B | $Br^-$ | 0.57 | 0.56 |
| Cl-B | $I^-$ | 0.62 | 0.76 |
| Cl-B | $CuCl_2^-$ | 0.50 | 0.66 |
| Cl-B | $CuBr_2^-$ | 0.57 | 0.54 |
| Cl-B | $CuI_2^-$ | | 0.69 |
| CF | $Cl^-$ | 0.54 | 0.65 |
| CF | $Br^-$ | 0.59 | 0.71 |
| CF | $I^-$ | 0.72 | 0.53 |
| | ave. | 0.64 | 0.58 |

a. Solvents: T, toluene; B, benzene; Cl-B, chlorobenzene; CF, chloroform.

agreement with the values obtained in this work.

The differences in log $K_{ex}$ between extracting solvents are summarized in Table 4. The order of log $K_{ex}$ was chloroform>chlorobenzene>benzene>toluene. The differences in log $K_{ex}$ between chloroform and chlorobenzene for $X^-$ and $CuX_2^-$ averaged 2.96 and 0.90, respectively: the difference in the value of $\Delta$log $K_{ex}$ between $X^-$ and $CuX_2^-$ is very large. This may be caused by the effect of the solvation of chloroform on the anions:[9-11] halide ions are more solvated by chloroform than dihalogenocuprate(I) complex ions are. Thus, the halide ions are more easily extracted into chloroform. The values of $\Delta$ log $K_{ex}$ between chlorobenzene and benzene for iodide and diiodocuprate(I) ions were 1.66 and 1.85, and those between benzene and toluene for the same anions were 0.56 and 0.47: in both cases, the values of $\Delta$log $K_{ex}$ for iodide ion are nearly equal to those for diiodocuprate(I) ion.

The results of the extractability and the contribution of some factors to the extraction constants obtained in this work are useful for designing the novel extraction systems for the separation and the determination method.

Table 4 Differences in log $K_{ex}$, $\Delta$ log $K_{ex}$, between extracting solvents

| Anions | Cations | $\Delta$ log $K_{ex}$[a] CF–Cl-B | Cl-B–B | B–T |
|---|---|---|---|---|
| $X^-$ | | | | |
| $Br^-$ | MEP | 3.06 | | |
| $I^-$ | MEP | 2.92 | | |
| $Cl^-$ | EEP | 2.92 | | |
| $Br^-$ | EEP | 3.21 | | |
| $I^-$ | EEP | 2.69 | | |
| $Cl^-$ | PEP | 2.83 | | |
| $Br^-$ | PEP | 3.23 | | |
| $I^-$ | PEP | 2.79 | 1.66 | 0.56 |
| | ave. | 2.96±0.27 | 1.66 | 0.56 |
| $CuX_2^-$ | | | | |
| $CuCl_2^-$ | MEP | 0.92 | | |
| $CuBr_2^-$ | MEP | 0.88 | | |
| $CuI_2^-$ | MEP | | 1.73 | 0.30 |
| $CuI_2^-$ | EEP | | 1.96 | 0.49 |
| $CuI_2^-$ | PEP | | | 0.61 |
| | ave. | 0.90±0.02 | 1.85±0.11 | 0.47±0.15 |

a. Difference in log $K_{ex}$ between two extracting solvents: CF, chloroform; Cl-B, chlorobenzene; B, benzene; T, toluene.

*Extraction-spectrophotometric method of copper based on the formation of an ion association complex of dihalogenocuprate(I) with azo-dye cations*

From the results in Tables 1–4, the two most likely extraction systems for a spectrophotometric method of copper were selected: they are the one using MEP, iodide ion and chlorobenzene, and the one using PEP, bromide ion and chlorobenzene. Figure 4 shows the extraction percent for $CuBr_2^-$ and $Br^-$ with PEP and chlorobenzene, calculated from each extraction constant. Though the extraction percent of $CuBr_2^-$ and $Br^-$ is nearly 100% and 0% in the region of the values of log[$PEP^+$] from −2 to −1, the absorbance of the reagent blank is large at this concentration of PEP, because of the large concentration of bromide ion. As a compromise, the condition of $3\times10^{-4}$ M PEP was selected, though the extraction percent of dibromocuprate(I) ion is about 85% at that concentration of PEP. The same consideration can be done for the $MEP^+\cdot CuI_2^-$ – chlorobenzene extraction system.

Experimental conditions for the determination of copper and the molar absorptivities obtained are shown in Table 5. Both the observed and the calculated absorbances of the reagent blanks are also shown in Table 5: they are in good agreement with each other. From the results obtained by the calculations and the experiments, the method with PEP and bromide ion is

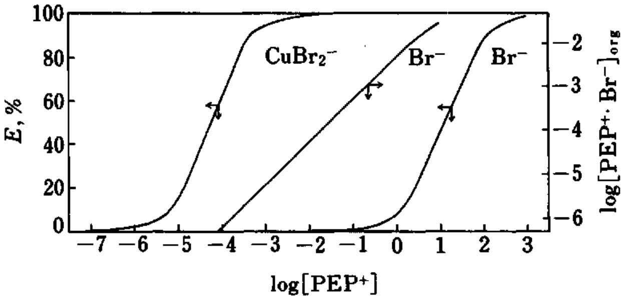


Fig. 4 Percentage extraction of $Br^-$ and $CuBr_2^-$, and the concentration of the ion associate, $PEP^+\cdot Br^-$, in chlorobenzene as a function of the concentration of PEP. $[Br^-]_{initial}$=0.03 M.

Table 5 The molar absorptivities ($\varepsilon$) of ion association complexes of dihalogenocuprate(I) with azo-dye cations extracted into chlorobenzene

| Azo dye | Ligand ($X^-$) | $[X^-]_{initial}$/M | $[Dye]_{initial}$/M | $\lambda_{max}$/nm | Absorbance of reagent blank Obs.[a] | Calc.[b] | $\varepsilon/10^4$ l mol$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| MEP | $I^-$ | 0.01 | $1.5\times10^{-4}$ | 575 | 0.153 | 0.130 | 5.7 |
| PEP | $Br^-$ | 0.03 | $3.0\times10^{-4}$ | 575 | 0.111 | 0.115 | 6.0 |

a. Obs.=observed value. b. Calc.=value calculated from the extraction constant of halide ion and the molar absorptivity of azo dye.

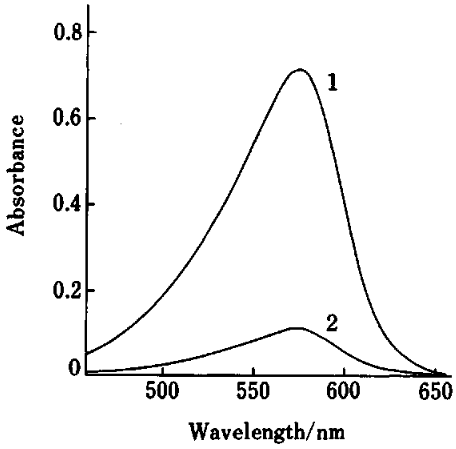


Fig. 5 Absorption spectra of the ion association complex of dibromocuprate(I) with the $C_3H_7$-derivative of the azo dye(PEP) in chlorobenzene. $[Br^-]_{initial}=0.03$ M. $[PEP]_{initial}=3\times10^{-4}$ M. Curve 1: $5\times10^{-6}$ M copper; 2: reagent blank; reference: chlorobenzene.

preferable. Figure 5 shows the absorption spectra obtained with PEP and bromide ion.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 63303004).

## References

1. S. Motomizu and K. Tôei, *Bunseki Kagaku*, **27**, 213 (1978).
2. S.-C. Rui, S. Motomizu and K. Tôei, *Bunseki Kagaku*, **34**, 643 (1985).
3. Z. Marczenko, *Mikrochim. Acta*[Wien], **1977**, 651.
4. K. Yamamoto and S. Motomizu, *Analyst* [London], **112**, 1011 (1987).
5. K. Yamamoto and S. Motomizu, *Bunseki Kagaku*, **36**, 343 (1987).
6. S. Motomizu, Y. Hazaki, M. Oshima and K. Tôei, *Anal. Sci.*, **3**, 265 (1987)
7. K. Higuchi, S. Monya, Y. Shimoishi, H. Miyata and K. Tôei, *Bunseki Kagaku*, **29**, 180 (1980).
8. S. Motomizu, *Bunseki Kagaku*, **33**, 31 (1984).
9. G. Schill, in "*Ion Exchange and Solvent Extraction*", Vol. 6, p. 11, ed. J. A. Marinsky and Y. Marcus, Chap. 1. Marcel Dekker, New York, 1974.
10. R. Modin and G. Schill, *Talanta*, **22**, 1017 (1975).
11. G. Schill "*Separation Methods for Drugs and Related Organic Compounds*", p. 14, Apotekarsocieteten, Stockholm, 1978.
12. S. Motomizu and K. Tôei, *Anal. Chim. Acta*, **120**, 267 (1980).

(Received December 15, 1988)
(Accepted February 6, 1989)