# CONCENTRATION OF COPPER(II) ION BY LIQUID MEMBRANE WITH BATHOCUPROINE

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**The distribution ratios of copper(II) ion between an aqueous solution containing a copper salt in the presence of nitrate, chloride or sulfate and an organic phase containing 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) in 1,2-dichloroethane (DCE) were measured as a fundamental study for establishing the liquid membrane system.**

**The difference in distribution ratio between nitrate and sulfate used in large excess was applied to drive the uphill transport of copper ion. The liquid membrane process consisted of the DCE solvent containing bathocuproine as a transport carrier and the two aqueous copper ion solutions containing a large excess of nitrate and sulfate ions. In this process, reproducible rate data were obtained by using a liquid-film holder in which the liquid membrane was maintained at constant pressure between two sheets of hydrophilic filter to prevent its leakage. The transport rate was examined by the quasi-steady model based on the three mass transfer steps involving a series of formation and dissociation of the copper-bathocuproine ion-pair with nitrate anion that take place instantaneously and reversibly at both interfaces of the liquid membrane. As a result, it became clear that copper ion was concentrated by the extraction through one hydrophilic filter, the diffusion of ion-pair across the liquid membrane and the back-extraction through the opposite filter accompanying the pseudo-first order equilibrium reaction for the complexation of copper with sulfate ion.**

## Introduction

The permeation of a solute through a liquid membrane containing a mobile carrier[1,5,8] is a new separation technique. A noteworthy investigation of its applications, the uphill transport of Cu(II) ion through a bulk 1,2-dichloroethane (DCE) membrane containing 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) was reported by Sugiura and Shinbo.[13] This transport is driven by the concentration gradient of copper-bathocuproin ion-pair across the membrane, which arises from a difference in distribution ratios based on anionic species. Although copper transport with chelating agents such as LIX 65N and SME 529 based on a pH gradient across the membrane has been reported,[3,14] transport based on the anionic species, which is suitable for carrying out the selective separation of copper from a solution, has not been sufficiently investigated.

In this work, the separation and concentration of Cu(II) ion were studied to clarify the permeation process through the DCE liquid membrane containing bathocuproine as a mobile carrier from the viewpoint of equilibrium and kinetics. To obtain reproducible data, the transport rate of Cu(II) ion was measured through a liquid membrane, held between two sheets of hydrophilic filter, that separates two well-stirred solutions containing the mixtures $Cu(NO_3)_2$–$KNO_3$ and $CuSO_4$–$K_2SO_4$ respectively.

## 1. Experimental

### 1.1 Materials

An organic solution of $2\times10^{-2}$ kmol/m$^3$ concentration was prepared by dissolving bathocuproine obtained from Kanto Kagaku Co. Ltd. in water-saturated DCE. From this, organic solutions of other concentrations below $5\times10^{-3}$ kmol/m$^3$ were obtained by further dilution. The aqueous solution was prepared by adding a mixture of copper and alkali metal salts to DCE-saturated water. All reagents were of reagent grade and were used without further purification, except for the recrystallization of copper sulfate (pentahydrate) from water.

### 1.2 Procedures

(1) Equilibrium studies The salt mixtures employed as the aqueous phase were mainly $Cu(NO_3)_2$–$K_2NO_3$, $CuCl_2$–KCl and $Cu(NO_3)_2$–$CuSO_4$–$K_2SO_4$ systems containing each copper salt at various concentrations below $2.5\times10^{-3}$ kmol/m$^3$ in the presence of a large excess of 0.1 or 0.3 kmol/m$^3$ alkali metal salt. Equal volumes (5 cm$^3$) of the above organic and

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aqueous phases were transferred into a stoppered glass tube and shaken mechanically in a thermostated water bath at 25°C for about an hour. After equilibrium was reached, the two phases were centrifuged and then a certain portion was mainly sampled from the aqueous phase. Initial and equilibrium copper concentrations in the aqueous phase were determined by atomic adsorption spectrophotometry (Hitachi Model 180-50). In some experiments, the concentration of copper-bathocuproine complex in the organic phase was analyzed by the colorimetric method of copper(I)-bathocuproine complex.[12] The analytical value obtained agreed well with that estimated from the difference between the initial and equilibrium copper concentrations in an aqueous phase.

(2) Kinetic studies The experimental apparatus is shown in **Fig. 1**(a). The liquid-film holder used to support the liquid membrane was clamped between the upper and lower cells with inner diameter of 5 cm. The holder was constructed of two sheets of hydrophilic membrane filter, fixed between two pieces of 20-mesh stainless gauze with Teflon flange joint, as shown in Fig. 1(b). The membrane filter was the regenerated cellulose type (Advantic Toyo Ltd.; thickness 110 $\mu$m, pore size 0.8 $\mu$m, porosity 71%). After these two filters were conditioned by soaking them in pure water, the DCE solvent containing bathocuprione used as the liquid membrane was held between the two filters in the holder, by introducing it from a storage tank to a constant-head tank through a fine Teflon tube of 0.2 cm i.d.

Since the filters are water-wetted, the capillary forces tend to cause water to penetrate the liquid membrane between the two filters, though the liquid membrane does not leak out of the filter surfaces. To counteract this tendency, it was necessary to increase the pressure in the holder by maintaining the liquid level in the head tank above that in the upper cell after both cells were filled with each aqueous phase, as shown in Fig. 1(a). Under the given pressure, the holder was filled with about 2.6 $cm^3$ of the liquid membrane (effective thickness of liquid membrane between the two filters; $l_m = 0.133$ cm) when the Teflon plugs at its inlet and outlet were closed during the course of the experiment.

The aqueous solution containing $Cu(NO_3)_2$ at various concentrations and 0.1 $kmol/m^3$ $KNO_3$ was poured into the lower cell by excluding all air, and then the aqueous solution containing $CuSO_4$ at the same concentration as $Cu(NO_3)_2$ in the lower cell and 0.1 $kmol/m^3$ $K_2SO_4$ was poured into the upper cell. Both aqueous solutions (100 $cm^3$ each) previously saturated with DCE were agitated independently by two flat-blade stirrers in the same direction at the same velocity of 420 rpm. Each cell was maintained at 25°C by circulation of thermostated water through

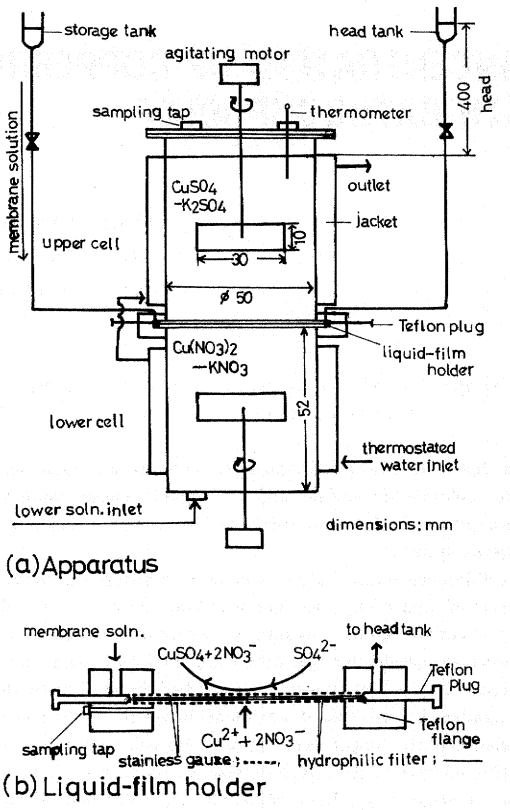



**Fig. 1.** Experimental apparatus (a) and liquid-film holder (b)

the jacket.

The transport rates were measured by varying the concentrations of copper salt and carrier, both of which were below $2.5 \times 10^{-3}$ $kmol/m^3$. The copper concentrations were measured at regular intervals by the atomic adsorption method, after a sample of 0.5 $cm^3$ was taken with a syringe from each cell by replacing it with each starting solution. The initial rate was calculated by the following equation.

$$J_0 = -(V/A)(dCt_{b1}/dt)_{t=0} \quad (1)$$

## 2. Experimental Results and Discussion

### 2.1 Equilibrium studies

(1) Composition of copper complex The composition of copper-bathocuproine complex, which had not previously been fully examined, was determined by the method of continuous variation for $Cu(NO_3)_2$–$KNO_3$ and $CuCl_2$–KCl systems. In **Fig. 2**, maximum extraction occurs at the point corresponding to $Ct_0/(Ct_0 + \bar{C}_{L,0}) = 1/3$, when the total concentration of copper and bathocuproine (L) was kept constant as $Ct_0 + \bar{C}_{L0} = 10^{-3}$ $kmol/m^3$ and the extraction was then made with varying molar ratios of copper salt to bathocuproine in the presence of a large excess of 0.1 $kmol/m^3$ alkali metal salt. From this, it is found that the combination ratio of bathocuproine to copper is of a 1 : 2 stoichiometry. Thus, the ion-pair of $\overline{CuL_2X_2}$ type is extracted into the organic phase in the

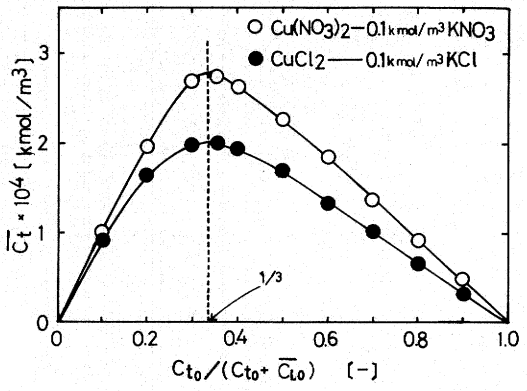



**Fig. 2.** Continuous variation plots; $Ct_0+\overline{C}_{L_0}=10^{-3}$ kmol/m$^3$=const.

presence of univalent anion ($X^-$). This type is identical with that of other phenanthroline derivatives already reported: 4,7-diphenyl[7] and 2,9-dimethyl-1,10-phenanthroline.[16] For the $CuSO_4$–$K_2SO_4$ system, however, the extraction of copper was almost negligible.

(2) Distribution ratio When only $\overline{CuL_2X_2}$ type is extracted in the presence of a large excess of $X^-$, the extraction equilibrium may be expressed as follows:

$$Cu^{2+}+2\bar{L}+2X^-=\overline{CuL_2X_2} \qquad (2)$$

$$K_{ex}=[\overline{CuL_2X_2}]/[Cu^{2+}][X^-]^2\bar{C}_L^2 \qquad (3)$$

This treatment is based on the assumption that bathocuproine and ion-pair are almost insoluble in the aqueous phase.[15] For this, no adsorption spectra of these components were observed in the aqueous phase by the spectrophotometric method. In addition, $CuX_2$ and KX were regarded as completely dissociated electrolytes.

When the concentration $[X^-]$ is kept constant by use of a large excess of each alkali metal salt, the distribution ratio for Eq. (2) is expressed as

$$D=\bar{C}t/Ct=[\overline{CuL_2X_2}]/[Cu^{2+}]=K'_{ex}\bar{C}_L^2 \qquad (4)$$

where $K'_{ex}=K_{ex}[X^-]^2$ given by $[X^-]\fallingdotseq[KX]_0$ ($[KX]_0$: amount of added alkali metal salt) and $\bar{C}_L=\bar{C}_{L0}-2\bar{C}t=\bar{C}_{L0}-2(Ct_0-Ct)$ from the mass balance when the volumes of organic and aqueous phases are equal.

On the other hand, copper ion in the back-extraction step is stripped with $X^-$ into an aqueous phase containing a large excess of $SO_4^{2-}$ by the dissociation of $CuL_2X_2$. In this case, the extraction of copper with $X^-$ is depressed by the complexation[2,10] of copper ion with $SO_4^{2-}$ in the aqueous phase, as given by

$$Cu^{2+}+SO_4^{2-}=CuSO_4 \qquad (5)$$

$$\beta=[CuSO_4]/[Cu^{2+}][SO_4^{2-}] \qquad (6)$$

Here, further complexation such as $Cu(SO_4)_2^{2-}$ was neglected since the stability of the complex is very low in the aqueous phase of 0.1 kmol/m$^3$ $K_2SO_4$.[10]

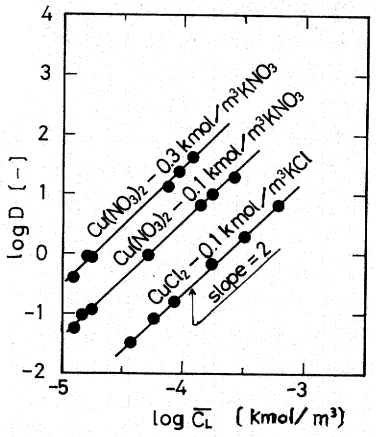



**Fig. 3.** Plots of $\log D$ vs. $\log\overline{C}_L$ for $Cu(NO_3)_2$ and $CuCl_2$ systems

**Table 1.** Extraction constants

| System | $K_{ex}$ [m$^{12}$/kmol$^4$] |
|---|---|
| $Cu(NO_3)_2$–0.1 kmol/m$^3$ $KNO_3$ | $2.91\times10^{10}$ |
| $Cu(NO_3)_2$–0.3 kmol/m$^3$ $KNO_3$ | $3.30\times10^{10}$ |
| | av. $3.12\times10^{10}$ |
| $CuCl_2$–0.1 kmol/m$^3$ KCl | $2.05\times10^{9}$ |

When the concentration $[X^-]$ is changed in the presence of a large excess of $SO_4^{2-}$, the distribution ratio of copper is described by Eqs. (4)–(6) as

$$D=\bar{C}t/Ct=[\overline{CuL_2X_2}]/([Cu^{2+}]+[CuSO_4])$$
$$=(K_{ex}/m)[X^-]^2\bar{C}_L^2 \qquad (7)$$

where

$$m=(1+\beta[SO_4^{2-}])=\text{a constant} \qquad (8)$$

For the $Cu(NO_3)_2$–0.1 and 0.3 kmol/m$^3$ $KNO_3$ and the $CuCl_2$–0.1 kmol/m$^3$ KCl systems, each distribution ratio was measured by varying the carrier and copper salt concentrations.

In **Fig. 3**, the plots of $\log D$ against $\log\bar{C}_L$ are shown according to Eq. (4). In the measured regions for $\bar{C}_{L0}\leqq5\times10^{-3}$ and $Ct_0\leqq2.5\times10^{-3}$ kmol/m$^3$, $D$ is proportional to $\bar{C}_L^2$. From these results, each extraction constant for the two systems is shown as $K_{ex}=K'_{ex}/[X^-]^2$=const. in **Table 1**. For the $Cu(NO_3)_2$–$KNO_3$ system, the mean of $K_{ex}$, $3.12\times10^{10}$ m$^{12}$/kmol$^4$, was adopted because there is no significant difference between 0.1 and 0.3 kmol/m$^3$ $KNO_3$. It was also found that the extractability in the presence of anion species decreases in the general order with respect to extraction of ion-pair as: $NO_3^->Cl^-\gg SO_4^{2-}$.[13]

For the $Cu(NO_3)_2$–$5\times10^{-4}$ kmol/m$^3$ $CuSO_4$–0.1 kmol/m$^3$ $K_2SO_4$ system, the distribution ratio was

measured by varying concentrations of $Cu(NO_3)_2$ at $\bar{C}_{L0}=2\times10^{-3}$ kmol/m$^3$ to clarify the effect of $SO_4^{2-}$ on the distribution ratio.

In **Fig. 4** a plot of $D/[X^-]^2\bar{C}_L^2$ vs. $[Cu(NO_3)_2]_0$ is shown by taking $Ct_0=[Cu(NO_3)_2]_0+[CuSO_4]_0$ and $[X^-]=2([Cu(NO_3)_2]_0-\bar{C}t)$. As may be expected from Eq. (7), the value of $D/[X^-]^2\bar{C}_L^2$ was obtained as a constant equal to $K_{ex}/m=1.34\times10^{10}$ m$^{12}$/kmol$^4$. Thus, with the observed value of $K_{ex}$, $m=2.33$—which brings about a lowering of the distribution ratio—and $\beta=13.3$ m$^3$/kmol at $[SO_4^{2-}]=0.1$ kmol/m$^3$ (ionic strength $=0.3$ kmol/m$^3$) were obtained. This value of $\beta$ agreed well with that calculated from the thermodynamic constant (200 m$^3$/kmol),[2] by considering the change in activity due to ionic strength.

### 2.2 Kinetic studies

(1) Transport Rate From the lower cell, copper ions diffuse through the pores within one hydrophilic filter impregnated with the solution containing a large excess of $NO_3^-$ and is extracted into the liquid membrane by forming $\overline{CuL_2(NO_3)_2}$ with carrier. This ion-pair diffuses across the membrane and then copper ion is liberated with $NO_3^-$ into the upper cell through the other filter by the dissociation of $\overline{CuL_2(NO_3)_2}$ and the formation of $CuSO_4$, as shown Fig. 1(b). By the dissociation of ion-pair, the carrier regenerated in the membrane returns to its original state and repeats the transport of copper mentioned above. Such a process is divided into three steps in series, due to the extraction of copper through the lower filter, the diffusion of $\overline{CuL_2(NO_3)_2}$ across the membrane and the back-extraction of copper through the upper filter accompanying the formation of $CuSO_4$. The reaction for $CuSO_4$ may be regarded as a psuedo-first order equilibrium reaction with respect to copper ion when the upper filter is impregnated with the solution containing a large excess of $SO_4^{2-}$. Since the copper salt is insoluble in the membrane and the solubility of ion-pair in aqueous phase is neglected as well as the carrier, the formation and dissociation of ion-pair take place reversibly at each interface of the membrane.

When copper diffusion through these steps is so slow that the quasi-steady state may be assumed, the following simplified transport rate in terms of total copper concentration ($Ct$) is used according to the film model through the two stirred cells:

$$\begin{aligned}-dCt_{b1}/dt&=dCt_{b2}/dt\\&=k_wa(Ct_{b1}-Ct_{i1})\\&=k_ma(\bar{C}t_{i1}-\bar{C}t_{i2})\\&=k_wap'(Ct_{i2}-Ct_{b2})\end{aligned}\qquad(9)$$

where $p'$ refers to the reaction factor in terms of $Ct=[Cu^{2+}]+[CuSO_4]$ for the pseudo-first order equilibrium reaction through back-extraction, which is given

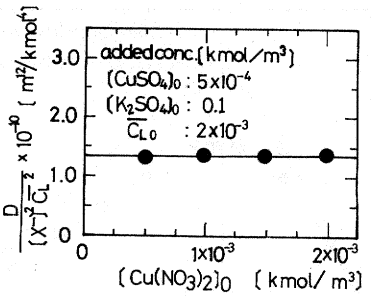



**Fig. 4.** Effect of $Cu(NO_3)_2$ concentration on distribution ratio for $Cu(NO_3)_2$–$CuSO_4$–$K_2SO_4$ system

by[9]

$$p'=p/m=\text{a constant}\qquad(10)$$

and $p$ is the reaction factor in terms of $[Cu^{2+}]$ only;

$$p=[1+(D_{f,S}/D_{f,X})\beta[SO_4^{2-}]_{b2}]\qquad(11)$$

With $m=2.33$ at $[SO_4^{2-}]_{b2}=0.1$ kmol/m$^3$ obtained before, $p=1.93$ and $p'=0.829$ can be estimated by expressing as $D_{f,S}=8.54\times10^{-10}$ and $D_{f,X}=1.22\times10^{-9}$ m$^2$/s[11] with the diffusivities of $CuSO_4$ and $Cu(NO_3)_2$, respectively.

For the formation and dissociation of ion-pair at both interfaces, these rates may be assumed to be rapid enough to be equilibrated, if the kinetics is the same as that of Cu(II)-phenanthroline measured by the stopped-flow method.[4] Therefore, the following relations based on Eqs. (4) and (7) are applicable to the expressions of interfacial concentrations on both sides.

$$\frac{\bar{C}t_{i1}}{Ct_{i1}}=\frac{[\overline{CuL_2X_2}]_{i1}}{[Cu^{2+}]_{i1}}=K'_{ex}(\bar{C}_{L0}-2\bar{C}t_{i1})^2\qquad(12)$$

$$\begin{aligned}\frac{\bar{C}t_{i2}}{Ct_{i2}}&=\frac{[\overline{CuL_2X_2}]_{i2}}{[Cu^{2+}]_{i2}(1+\beta[SO_4^{2-}]_{b2})}\\&=(K_{ex}/m)[X^-]_{i2}^2(\bar{C}_{L0}-2\bar{C}t_{i2})^2\end{aligned}\qquad(13)$$

Here, the carrier concentration at each interface was taken as $\bar{C}_{Li}=\bar{C}_{L0}-2\bar{C}t_i$, which is the same as before.

From Eq. (9), the following relations are obtained when the initial concentrations of total copper ($Ct_0$) in both cells are equal;

$$2Ct_0=Ct_{b1}+Ct_{b2}\qquad(14)$$

$$a=k_w/k_m=(\bar{C}t_{i1}-\bar{C}t_{i2})/(Ct_{b1}-Ct_{i1})\qquad(15)$$

$$p'=(Ct_{b1}-Ct_{i1})/(Ct_{i2}-Ct_{b2})\qquad(16)$$

On the other hand, anion $X^-$ corresponding to twice the increment of the total copper is liberated stoichiometrically with $Cu^{2+}$ through the upper filter. Hence, $Ct_{i2}$ and $[X^-]_{i2}$ are expressed from Eqs. (14) and (16) as follows:

$$Ct_{i2}=(Ct_{b1}-Ct_{i1})/p'+(2Ct_0-Ct_{b1})\qquad(17)$$

$$[X^-]_{i2} = 2(Ct_{i2} - Ct_0)$$
$$= 2[(Ct_{b1} - Ct_{i1})/p' + (Ct_0 - Ct_{b1})] \quad (18)$$

By introducing $Ct_{i2}$ and $[X^-]_{i2}$ into Eq. (13), $\bar{C}t_{i2}$, which is a root of the quadratic equation, is obtained as a function of $Ct_{i1}$, as well as $\bar{C}t_{i1}$ given by Eq. (12), and so the $\alpha$ value of Eq. (15) is expressed in terms of $Ct_{i1}$ alone when $Ct_0$ and $Ct_{b1}$ are the known values.

Thus, the simultaneous solution of $Ct_{i1}$ to the bulk concentration $Ct_{b1}$ to satisfy Eqs. (12), (13) and (15) can be numerically computed for a fixed value of $\alpha$ and at the same time, Eq. (9) can be numerically integrated with the initial condition of $Ct_{b1} = Ct_{b2} = Ct_0$ at $t=0$, to obtain the time-dependent concentrations of total copper in both cells when $k_w$, $k_m$, $a = (A/V)$ and the reaction factor ($p'$) are given.

(2) Time-dependent concentration of copper ion The time-dependent concentrations of copper ion in the lower and upper cells measured by varying only $\bar{C}_{L0}$ at $Ct_0 = 10^{-4}$ kmol/m$^3$ are shown with the fraction of copper ion in **Fig. 5**. In this experiment, reproducible data were obtained even when the measurements were repeated over eight times without replacing the liquid membrane under the same conditions. The curve of $Ct_{b1}/Ct_0$ for the lower cell decreases with the increase in $Ct_{b2}/Ct_0$ for the upper cell, because the accumulation of copper ion within the liquid membrane can be neglected. As a result, the analysis based on the quasi-steady approximation was made with only the curves of $Ct_{b1}/Ct_0$ vs. time for the lower cell, for which $Ct_0$ is changed at $\bar{C}_{L0} = 2 \times 10^{-3}$ kmol/m$^3$, as shown in **Fig. 6**.

(3) Mass transfer coefficients Based on Eq. (1), the initial flux $J_0$ was evaluated from the slope of each straight line near time zero in Figs. 5 and 6, and is plotted against $Ct_0$ or $\bar{C}t_{i1,t=0}$ in **Fig. 7**.

The value of $J_0$ begins to rise in proportion to $Ct_0$ or $\bar{C}t_{i1,t=0}$ obtained numerically with the initial values of $Ct_{b1} = Ct_0$ and $\bar{C}_{L0}$, and then approaches a constant value. This means that the rate-controlling step varies with the increase in $Ct_0$ or $\bar{C}t_{i1,t=0}$. Therefore, from the data in the region where the initial flux is given by $J_0 \fallingdotseq k_w Ct_0$ in the case of $\alpha \to 0$ (controlling step through lower filter) or $J_0 \fallingdotseq k_m \bar{C}t_{i1,t=0}$ in the case of $\alpha \to \infty$ (controlling step through membrane), each mass transfer coefficient was evaluated as $k_w = 2.04 \times 10^{-6}$ or $k_m = 3.10 \times 10^{-7}$ m/s at 420 rpm.

If the transport of copper through the lower filter is dependent on the two transfer resistances through the aqueous film at its interface and the tortuous pore within the hydrophilic filter, which are denoted in terms of the mass transfer coefficients, $k_{wf}$ and $k_{hf}$, respectively, $k_w$ may be expressed as

$$1/k_w = 1/k_{wf} + 1/k_{hf} \quad (19)$$

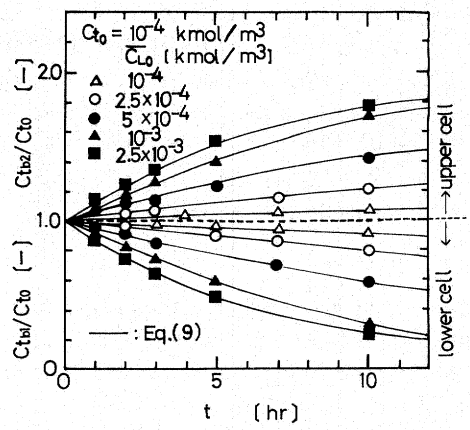



**Fig. 5.** Experimental and calculated variations of copper ions in both cells with time; the calculation was made with $k_w = 2.04 \times 10^{-6}$ m/s, $k_m = 3.10 \times 10^{-7}$ m/s, $a = (A/V) = 19.6\,\mathrm{m}^{-1}$ and $p' = 0.829$

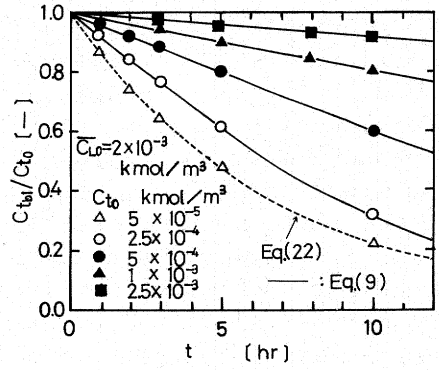



**Fig. 6.** Experimental and calculated variation of copper ions in lower cell with time; the calculation was made with the same values used in Fig. 5

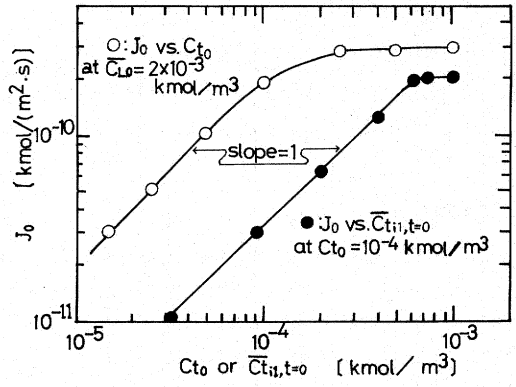



**Fig. 7.** Effect of concentration of copper salt or carrier on initial flux

where $k_{hf} = D_{f,x}/l\tau$ and $\tau$ is a membrane constant of the hydrophilic filter covered with a piece of stainless gauze.

The value of $k_{wf}$ was estimated as $9.52 \times 10^{-5}$ m/s by measuring the dissolution rate of benzoic acid from a flat surface into pure water in the upper cell under the same conditions as used in the measurement of $k_w$. In this case, the mass transfer coefficient for

benzoic acid was obtained as $8.34\times10^{-5}$ m/s and was converted to $k_{wf}$ for $Cu(NO_3)_2$ by the relation[6] $k_{wf}\propto D_f^{2/3}$. The values of diffusivity for benzoic acid and $Cu(NO_3)_2$ in the aqueous phase were adopted as $1.0\times10^{-9}$ m$^2$/s[11] and $1.22\times10^{-9}$ m$^2$/s, respectively.

Using the above values of $k_{wf}$ and $k_w$, the $k_{hf}$ value in Eq. (19) was obtained as follows.

$$k_{hf}=D_{f,\mathrm{X}}/l\tau=2.08\times10^{-6}\ \mathrm{m/s} \qquad (20)$$

From this result, it is seen that the permeation rate is controlled solely by the diffusional resistance through the filter because $k_w\fallingdotseq k_{hf}$. Furthermore, the membrane constant $\tau$ was calculated as 5.33 [—] with $D_{f,\mathrm{X}}=1.22\times10^{-9}$ m$^2$/s and $l=110\ \mu$m. This value is close to that in the lipophilic Teflon filter reported previously.[5]

For the observed $k_m=3.1\times10^{-7}$ m/s, it is found to be not so different from $\bar{D}_f/l_m=3.55\times10^{-7}$ m/s, which was calculated from the thickness of the membrane, $l_m=0.133$ cm, and the diffusivity of ion-pair in DCE, $\bar{D}_f=4.72\times10^{-10}$ m$^2$/s estimated from Wilke and Chang's equation.[17]

With the observed values of $k_w$ and $k_m$, the time-dependent concentrations of copper ions calculated from the numerical procedure are shown by the solid lines in Figs. 5 and 6, which are in good agreement with the observed results. If the flux is limited by $J\fallingdotseq k_wCt_{\mathrm{b1}}$ when $\alpha\to0$, throughout the course of the transport process, the following equation is used:

$$-dCt_{\mathrm{b1}}/dt=k_waCt_{\mathrm{b1}} \qquad (21)$$

Integrating this equation with $Ct_{\mathrm{b1}}=Ct_0$ at $t=0$ gives

$$Ct_{\mathrm{b1}}/Ct_0=\exp(-k_wat) \qquad (22)$$

For the case of $Ct_0=5\times10^{-5}$ kmol/m$^3$ in Fig. 6, this condition is satisfied so that the broken curve calculated from Eq. (22) coincides with the observed data.

## Conclusion

Copper [II] ion is extracted into DCE organic phase, forming a ion-pair of $\overline{CuL_2X_2}$ type with bathocuproine and univalent anion, $X^-$, while the extractability of copper in the presence of a large excess of $SO_4^{2-}$ is negligibly small and is depressed by the complexation of copper ion with $SO_4^{2-}$ in the aqueous phase.

Such a difference in extractability based on two anionic species provides the driving force for the uphill transport of copper through a liquid membrane containing bathocuproine as a carrier. Much more stable transport operation is obtained by sandwiching the liquid membrane between two sheets of hydrophilic filter. The results for copper transport can be explained by the quasi-steady state model based on three diffusional resistances of copper species through the two hydrophilic filters and a liquid membrane.

### Nomenclature

| | | | |
|---|---|---|---|
| $A$ | = | interfacial area | [m$^2$] |
| $a$ | = | $A/V$ | [m$^{-1}$] |
| $C_L$ | = | concentration of bathocuproine in organic phase | [kmol/m$^3$] |
| $Ct$ | = | total concentration of copper species | [kmol/m$^3$] |
| $D$ | = | distribution ratio of copper species | [—] |
| $D_f$ | = | diffusivity | [m$^2$/s] |
| $D_{f,\mathrm{S}}$ | = | diffusivity of $CuSO_4$ in aqueous phase | [m$^2$/s] |
| $D_{f,\mathrm{X}}$ | = | diffusivity of $Cu(NO_3)_2$ in aqueous phase | [m$^2$/s] |
| $J$ | = | flux of copper species | [kmol/(m$^2\cdot$s)] |
| $K_{ex}$ | = | extraction constant of copper species | [m$^{12}$/kmol$^4$] |
| $K'_{ex}$ | = | $K_{ex}[\mathrm{X}^-]^2$ | [m$^6$/kmol$^2$] |
| $k_m$ | = | mass transfer coefficient of ion-pair in liquid membrane | [m/s] |
| $k_{hf}$ | = | mass transfer coefficient of aqueous phase through hydrophilic filter | [m/s] |
| $k_w$ | = | overall mass transfer coefficient defined by Eq. (19) | [m/s] |
| $k_{wf}$ | = | mass transfer coefficient in aqueous phase | [m/s] |
| $l$ | = | thickness of hydrophilic filter | [m] |
| $l_m$ | = | thickness of liquid membrane | [m] |
| $m$ | = | $(1+\beta[SO_4^{2-}]_{\mathrm{b2}})$ defined by Eq. (8) | [—] |
| $p$ | = | reaction factor defined by Eq. (11) | [—] |
| $p'$ | = | reaction factor defined by Eq. (10), $p/m$ | [—] |
| $t$ | = | time | [h] |
| $\alpha$ | = | $k_w/k_m$ | [—] |
| $\beta$ | = | stability constant defined by Eq. (6) | [m$^3$/kmol] |
| $\tau$ | = | membrane constant of hydrophilic filter | [—] |
| [ ] | = | concentration of chemical species | [kmol/m$^3$] |

〈Subscripts〉

| | | |
|---|---|---|
| 0 | = | initial state |
| 1 | = | lower cell |
| 2 | = | upper cell |
| b | = | species in bulk of aqueous phase |
| i | = | species adjacent to interface |

〈Superscripts〉

| | | |
|---|---|---|
| — | = | species in organic phase |

〈Chemical Species〉

| | | |
|---|---|---|
| L | = | bathocuproine used as ligand |
| X | = | univalent anion species |

### Literature Cited


1) Choy, E. M., D. F. Evans and E. L. Cussler: *J. Am. Chem. Soc.*, **96**, 7085 (1974).
2) Davis, C. W.: *J. Chem. Soc. (London)*, **140**, 2093 (1938).
3) Fujinawa, K., T. Morishita, M. Hozawa and H. Ino: *Kagaku Kogaku Ronbunshu*, **11**, 293 (1985).
4) Holyer, R. H., C. D. Hubbard, S. F. A. Kettle and R. G. Wilkings: *Inorg. Chem.*, **4**, 929 (1965).
5) Kataoka, T., T. Nishiki, Y. Tamura and K. Ueyama: *J. Chem. Eng. Japan*, **13**, 35 (1980).
6) Marangozis, J. and A. I. Johnson: *Can. J. Chem. Eng.*, **40**, 231 (1962).
7) Maruyama, K. and H. Tsukube: *Chem. Lett.*, 1133 (1981).
8) Moor, J. H. and R. S. Shechter: *AIChE J.*, **19**, 741 (1973).
9) Olander, D. R.: *AIChE J.*, **6**, 233 (1960).

10) Ringbom, A.: "Complexation in Analytical Chemistry," John Wiley and Sons Inc. (1963).
11) Sherwood, T. K., R. L. Pigford and C. R. Wilke: "Mass Transfer" in Chemical Engineering Series, McGraw-Hill (1975).
12) Smith, G. F. and D. H. Wilkins: *Anal. Chem.*, **25**, 510 (1953).
13) Sugiura, M. and T. Shinbo: *Bull. Chem., Soc. Jpn.*, **52**, 2209 (1979).
14) Takahashi, K., F. Ohtsubo and H. Takeuchi: *Kagaku Kogaku Ronbunshu*, **9**, 409 (1983).
15) Yamamoto, Y.: *Bunseki Kagaku*, **21**, 418 (1972).
16) Yamamoto, Y., T. Kumamaru, Y. Hayashi and M. Yamamoto: *Anal. Chem. Acta*, **69**, 321 (1974).
17) Wilke, C. R. and P. Chang: *AIChE J.*, **1**, 264 (1955).