**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Matina, Md.Abdul , Nomura, Masao , Fujii, Yasuhiko and Chen, Jingren(1998) 'Isotope Effects of Copper in Ligand-Exchange System and Electron-Exchange System Observed by Ion-Exchange Displacement Chromatography', Separation Science and Technology, 33: 8, 1075 — 1087

**To link to this Article: DOI:** 10.1080/01496399808545241

**URL:** http://dx.doi.org/10.1080/01496399808545241

SEPARATION SCIENCE AND TECHNOLOGY, 33(8), pp. 1075–1087, 1998

# Isotope Effects of Copper in Ligand-Exchange System and Electron-Exchange System Observed by Ion-Exchange Displacement Chromatography

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## ABSTRACT

Using cation- and anion-exchange resins, ion-exchange displacement chromatography of copper has been carried out to study the copper isotope effects in the ligand exchange system (LXS) and the electron exchange system (EXS), respectively. In the LXS, where malate was chosen as the ligand for $Cu^{2+}$ ions, the heavier isotope $^{65}Cu$ has been enriched at the front part of the copper chromatogram, which means that the heavier isotope $^{65}Cu$ is preferentially fractionated into the malate complex in the solution phase. In the EXS, where the Cu(I)/Cu(II) exchange reaction takes place in the HCl-anion exchanger resin system, the lighter isotope $^{63}Cu$ has been observed to be enriched at the Cu(I) chloride anion complex side. The result shows that the lighter isotope is preferentially fractionated into the anion exchange resin phase. The values of the single-stage separation coefficients ($\epsilon = S - 1$) of the $^{63}Cu/^{65}Cu$ isotopic pair have been calculated for LXS as $2.8 \times 10^{-4}$ at 40°C and for EXS as $3.8 \times 10^{-4}$ at 60°C.

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## INTRODUCTION

Taylor and Urey (1) first investigated the isotope separation of lithium using ion-exchange chromatography in 1938. Since then, many investigators have studied the isotope effects in chemical exchange not only on lighter elements such as lithium (2, 3), boron (4), carbon (5), nitrogen (6), etc., but also on heavier elements of calcium (7, 8), magnesium (9), strontium (10), zirconium (11, 12), uranium (13), etc.

These studies were made on the isotope effects appearing in a ligand-exchange system (LXS) where ligands are mainly exchanged between two different types of complexes of the concerned isotope ions whose valency state is unchanged. Copper isotope effects in LXS have not been reported although attempts were made on the measurement of isotope effects (14). A reported copper isotope study was on electromigration through a cation-exchange membrane (15).

In development work on uranium isotope separation by ion exchange in addition to the LXS, the electron-exchange system (EXS) has been intensively studied, specifically on the U(VI)–U(VI) redox system. Isotope effects in redox systems have recently been studied from the viewpoint of nucleus–electron interactions (16, 17). Since copper is a typical element of coordination chemistry and its ions form strong complex bonding with ligands, it is an appropriate ion to use for the study of isotope effects in LXS. In addition, copper has two ionic states, Cu(I) and Cu(II), in aqueous solutions. The present work deals with the isotope effects of both Cu(II)–ligand exchange and Cu(I)–Cu(II) exchange. The isotope effects in chemical exchange are determined by ion-exchange displacement chromatography in both LXS and EXS. Since the malic acid–eluent system has large separation coefficients among uranyl carboxylate complexes (18), in the present work (LXS) we apply malic acid as the ligand for the copper(II) complex formation system. Attention was placed on the analytical technique to obtain a reliable separation coefficient from the directly observed isotopic profile.

Copper is one of the trace elements essential to the healthy life of many plants as well as animals, usually occurring as part of the prosthetic group of oxidizing enzymes. These enzymes, high molecular weight proteins containing 0.05–0.35% copper, play a part in life's vital oxidation and reduction processes in which copper undergoes cyclic changes between the Cu(I) and Cu(II) states. Enriched Cu isotopes can be used as a tracer for the Cu reaction process. The development of a low-cost Cu isotope enrichment process would be helpful for such research work. In addition, the precise isotope analysis of copper made in the present work may be useful in life science.

# EXPERIMENTAL

## Ion-Exchange Resin and Reagents

The ion-exchange resin used in the LXS was a highly porous, high cross-linking (of 20%) type, strongly acidic cation-exchange resin (TITECH-3, 37–88 μm), and the resin used in the EXS was a highly porous anion-exchange resin (AR01, 30–60 μm). Both exchange resins were supplied by Asahi Chemical Industries. All reagents used were of analytical grade and were employed without further purification.

## Chromatographic Processes

A copper isotope separation experiment based on the malic acid LXS was carried out with a cyclic displacement chromatography system composed of three glass columns (0.8 cm inner diameter × 100 cm length, with water jackets) which were connected in series with a Teflon tube (1 mm inner diameter). These columns were packed uniformly with the strongly acidic cation-exchange resin (TITECH-3, 37–88 μm). The resin was pretreated with 2 M (mol/dm$^3$) HCl solutions to remove impurities and converted into the H$^+$ form. Then a 0.5 M $CuSO_4$ + 0.7 M $H_2SO_4$ solution was fed into the first column at a constant flow rate by a peristaltic pump to form a Cu$^{2+}$ adsorption band. When the Cu$^{2+}$ ion adsorption band had grown to be an appropriate length (20–25 cm), the supply of the feed solution was stopped. Then the Gd$^{3+}$ adsorption band and appropriate length of Gd$^{3+}$ ions were introduced into the column. The Gd$^{3+}$ and Cu$^{2+}$ adsorption bands were eluted by an eluent, D,L-malic acid ($COOH—CHOH—CH_2—COOH$) solution adjusted to pH 5.5 with a $NH_4OH$ solution. The eluent was fed at the same flow rate as the feed solution. The adsorption band of Cu$^{2+}$ was visible and blue, in contrast with the following pale brown Gd band. The three packed columns were repeatedly used in a merry-go-round way. After that the Cu$^{2+}$ adsorption band was eluted out from the last columns. The effluents were collected in small fractions and were subjected to concentration analysis and isotopic analysis.

In the EXS, two glass columns with the same size as used in the LXS were packed with an anion exchange resin (AR01, 30–60 μm). The resin of these columns was converted into Cl$^-$ form by feeding an HCl solution. Thereafter a Cu(I) chloro complex solution (0.2 M CuCl in 3 M HCl + 0.2 M $TiCl_3$ in 3 M HCl) was fed into the columns until the total resin was converted to the Cu(I) form. This Cu(I) adsorption band was eluted with ferric chloride solution (0.2 M $FeCl_3$ in 3 M HCl) at the flow rate of the feed solution. When the Cu(I) adsorption band was eluted out from the second column, the effluent

TABLE 1
Experimental Conditions in the Ligand-Exchange System and in the Electron-Exchange System

| System | Ligand-exchange system | Electron-exchange system |
|---|---|---|
| Resin | Strongly acidic cation-exchange resin (TITECH-3, 37–88μm) | Anion-exchange resin (AR01, 30–60μm) |
| Eluent | D,L-Malic acid 0.06 M adjusted by $NH_4OH$ at pH 5.5 | 0.2 M $FeCl_3$ in 3 M HCl |
| Feed solution | 0.5 M $CuSO_4$ + 0.7 M $H_2SO_4$ | 0.2 M CuCl in 3 M HCl + 0.2 M $TiCl_3$ in 3 M HCl |
| Column size | 0.8 cm I.D. and 100 cm length | Same as LES |
| Cu band length | 25 cm | — |
| Migration length | 14 m | 2 m |
| Temperature | 40°C | 60°C |
| Flow rate | 0.87 cm/min | 0.14 $cm^3$/min |
| Band velocity | 0.084 cm/min | 0.08 cm/min |
| Effluent volume | 6.262 $dm^3$ | 0.3 $dm^3$ |

was collected into small fractions, and the fractions were subjected to concentration analysis and isotopic analysis.

The temperatures of the columns were kept constant while in the eluent, operating at 40.0 ± 0.2°C in the LXS and at 60.0 ± 0.2°C in the EXS, by circulating the thermostatted water through the water jackets surrounding the columns. The experimental conditions for LXS and EXS are summarized in Table 1.

## Analysis

The concentration of Cu in each fraction of the effluents was determined by an ICP (inductively coupled plasma) photo-emission spectrometer, Shimadzu ICPS-50, at a 342.247 nm wavelength. The $^{63}Cu/^{65}Cu$ isotopic ratios of copper samples were determined by using a MAT 261 mass spectrometer with a thermal ionization method. The filament unit for sample ionization comprises two filaments made of rhenium ribbon; one is for sample vaporization and the other is for ionization. A drop of 20 μg copper sample was loaded on the surface of a vaporizing filament and dried by heating with an electric current of about 1.7 A for 1 minute. Then the sample filament unit was inserted into the ion source of the mass spectrometer. A Cu ion beam appeared when the ionization filament current reached ~1.7 A without using a vaporization current, and the $^{63}Cu$ and $^{65}Cu$ mass peaks were repeatedly recorded by a Faraday cup collector. The $^{63}Cu$ ion current was adjusted to 5–8 × $10^{-13}$

A. For the measurement of the isotopic ratio, the mass scanning of the pair of isotopes was repeated six times in a block and, in all cases, five blocks were recorded as one measurement. The isotopic ratios of a block were calculated by averaging all the peak height ratios of the recorded peaks of $^{63}Cu$ and $^{65}Cu$. The mass peaks recording time was approximately 1 hour and the total time for one measurement was about 2 hours.

## RESULTS AND DISCUSSION

### Ligand-Exchange System

The ion-exchange reactions involved in the LXS first takes place at the interface between the $Cu^{2+}$ and $Gd^{3+}$ adsorption bands. When the Gd complexes reach the rear bondary of the $Cu^{2+}$ adsorption band, the ligands are transferred from $Gd^{3+}$ to $Cu^{2+}$ ions because of the large stability constant of Cu–ligand complex formation (Eq. 1). During the downward move of the Cu–ligand complex species through the $Cu^{2+}$ adsorption band in the column, the isotopic exchange reaction takes place between $Cu^{2+}$ ions in the resin phase and the Cu–ligand complex species in the solution (Eq. 2). After that the CuLg complex reaches the $H^+$ ion band, where ligand are transferred to $H^+$ ions to form $H_2Lg$, and $Cu^{2+}$ ions are adsorbed in the resin phase (Eq. 3). The chemical reactions are expressed as

$$Gd_2Lg_3 + 3\underline{Cu}^{2+} \rightarrow 2\underline{Gd}^{3+} + 3CuLg \tag{1}$$

$$^{65}\underline{Cu}^{2+} + {}^{63}CuLg \rightleftharpoons {}^{63}\underline{Cu}^{2+} + {}^{65}CuLg \tag{2}$$

$$CuLg + 2\underline{H}^{+} \rightarrow \underline{Cu}^{2+} + H_2Lg \tag{3}$$

where Lg indicates ligand and the underlines represent the species in the resin phase.

The chromatogram of copper in the LXS after a migration of 14 m and the isotope abundance ratio observed in a displacement band are shown in Fig. 1. The "original" line shows the isotopic abundance ratio in the feed solution. It is seen that the heavier isotope, $^{65}Cu$, is preferentially fractionated into the front part, and the lighter isotope, $^{63}Cu$, into the rear part of the Cu adsorption band. This tendency is the same as that observed in the chromatographic isotope separation of calcium (7, 8), magnesium (9), and strontium (10).

The single stage separation factor, $S$ ($= 1 + \epsilon$) for the $^{63}Cu/^{65}Cu$ isotopic pair, is defined as

$$S = ([^{63}\underline{Cu}]/[^{65}\underline{Cu}])/([^{63}Cu]/[^{65}Cu]) \tag{4}$$

where an underline indicates the resin phase. The separation coefficient $\epsilon$ is calculated from the experimentally observed isotopic enrichment at the front

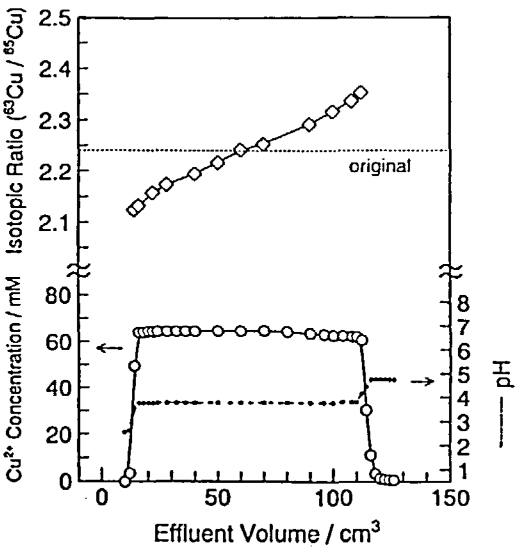

FIG. 1 Chromatogram and isotopic ratio curve of copper in the malate–ligand exchange system.

boundary or at the rear boundary of the chromatogram as previously reported (19, 20):

$$\begin{aligned} \epsilon &= \Sigma q_i|R_i - R_o|/QR_o(1 - R_o) \\ Q &= \Sigma q_i \quad \text{and} \quad q_i = C_iV_i \end{aligned} \tag{5}$$

where $q$ is the amount of copper in the sample fraction, $R$ is the atomic (molar) fraction of $^{63}$Cu, $Q$ is the total ion-exchange capacity of the resin for elemental copper under the experimental conditions, $C$ is the concentration of copper in the sample fraction, $V$ is the effective volume, and the subscripts $o$ and $i$ denote the original (feed solution) and the fraction number of the sample, respectively. The summation is taken over all the fractions for the front boundary part enriched in $^{63}$Cu or for the rear boundary part depleted of $^{63}$Cu.

Due to the small isotope effects of copper, long distance migration is necessary to measure the isotope separation coefficient. In such cases there would be a problem of remixing between the enrichment part and the depleted part according to the disappearance of the isotopic original plateau in the central part of the adsorption band. Apparently the isotope plateau regions has disappeared in Fig. 3. The value of $\epsilon$ was calculated from the front part of the chromatogram; $\epsilon_f$ from the front part is $1.93 \times 10^{-4}$ and $\epsilon_r$ from the rear part is $1.87 \times 10^{-4}$. The average value of $\epsilon_f$ and $\epsilon_r$ is $1.90 \times 10^{-4}$. The derived value of $\epsilon$ ($1.9 \times 10^{-4}$) is apparently underestimated due to remixing in the central part in the band. In the present work the estimation process is believed to yield a more reliable separation coefficient from the observed isotopic profile.

In the ideal cases of isotope enrichment by displacement chromatography with a sufficiently long isotopic plateau of the original value, the isotopic ratio, $r$, is described by (21)

$$\ln(r - r_o) = k(L - x) \tag{6}$$

where $r$ ($= R/1 - R$) is the isotopic ratio, $k$ is the slope coefficient, $L$ is the migration distance, $x$ is the distance from the starting point of the migration, and the subscript $o$ indicates the original or feed.

As expected from Eq. (6), when the isotopic ratios $\ln(r - r_o)$ are plotted against the migration distance, the plots shows a straight line with a slope of $k$. The plots of $\ln(^{65}r - {}^{65}r_o)$ (where $^{65}r = {}^{65}\text{Cu}/^{63}\text{Cu}$) for the front boundary and $\ln(^{63}r - {}^{63}r_o)$ (where $^{63}r = {}^{63}\text{Cu}/^{65}\text{Cu}$) for the rear boundary are presented in Fig. 2, where the mutually inverse isotopic ratios of $^{65}$Cu and $^{63}$Cu

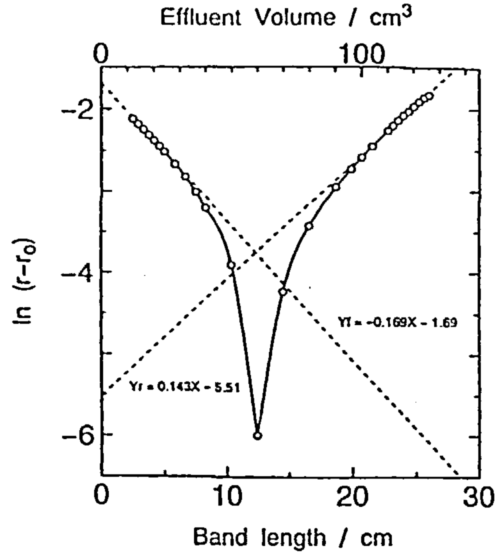

FIG. 2 The slope analysis of isotope enrichment in a copper adsorption band in the ligand exchange system. Yf and Yr represent the slope equations of the front part and rear part of the chromatogram, respectively, in the LXS.

are plotted since $r - r_o > 0$ is assumed in Eq. (6). In Fig. 2 it is clearly shown that the plots show the linear relations at both band boundary regions, while the plots significantly deviate from the linear relations in the middle part of the migration band.

On the assumption that the linear relations remaining in the boundary region can be extended to the directions inside the band, the theoretically estimated ideal isotopic profiles are drawn in Fig. 3 with dashed lines. Using the dashed lines, the estimated isotope separation coefficient $\epsilon_f$ for the front boundary can be calculated by the following equation (7) by using the observed slope of $k_f$ and the frontal isotopic ratio $r_p$ as

$$\epsilon_f = [(1 + r_o)/(k_f L)] \ln\{r_o(1 + r_p)/r_p(1 + r_o)\} \tag{7}$$

In the same way, the value of $\epsilon_r$ is calculated from the data for the rear boundary as

$$\epsilon_r = [(1 + r_o)/(k_f L r_o)] \ln\{(1 + r_p)/(1 + r_o)\} \tag{8}$$

The value of separation coefficients in the LXS calculated with the estimated data from the front part of the chromatogram (Fig. 3) is $2.6 \times 10^{-4}$ and that for the rear part is $3.0 \times 10^{-4}$. Thus the corrected value of $\epsilon_L$ in

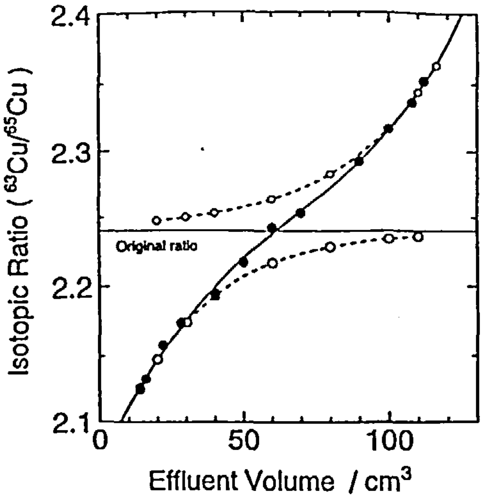

FIG. 3 The estimated theoretical isotopic profile derived for the experimental in the ligand exchange system. The filled circles represent the observed separation profile and the open circles represent the estimated separation profile in the LXS. Experimental conditions are given in Table 1.

TABLE 2
Directly Observed and Theoretically Estimated Separation Coefficients in the Ligand-Exchange System

| | Directly observed $\epsilon$ | Theoretically estimated $\epsilon$ |
|---|---|---|
| $\epsilon_f$ (front boundary) | $1.93 \times 10^{-4}$ | $2.6 \times 10^{-4}$ |
| $\epsilon_r$ (rear boundary) | $1.87 \times 10^{-4}$ | $3.0 \times 10^{-4}$ |
| $\epsilon_L$ (average) | $1.90 \times 10^{-4}$ | $2.8 \times 10^{-4}$ |

the present ligand exchange system is obtained by averaging the values of $\epsilon_f$ and $\epsilon_r$ as $2.8 \times 10^{-4}$. These $\epsilon$'s are summarized in Table 2. Since the heavier isotope is enriched in the complex species, the observed isotopic enrichment tendency agrees with the theoretically expected direction of the isotopic effects in chemical exchange.

## Electron-Exchange System

Cu(I) is a typical cation which forms strong coordination bonds with ligands such as amines, $Cl^-$, etc. In HCl solution, Cu(I) forms $CuCl_4^{3-}$ anions which are adsorbed in the anion-exchange resin. Cu(II) ions, on the other hand, do not form strong bonds with $Cl^-$ ions, and therefore the distribution coefficient of Cu(II) in the anion-exchange resin is small under the experimental conditions of the 3 M HCl solution. Due to the above-mentioned selectivity, Cu(I) ions are oxidized to Cu(II) and released from the anion-exchange resin when the Fe(III) eluent reaches the rear boundary of the Cu(I) adsorption band. The redox reaction taking place at the interface between the Cu(I) adsorption band and the Fe(III) eluent is given by

$$CuCl_4^{3-}\text{—}3R^+ + FeCl_6^{3-} + 3H^+ \rightarrow 3Cl^-\text{—}R^+ + CuCl_2 + FeCl_2 + 3HCl \tag{9}$$

where —$R^+$ is a fixed cation in the anion-exchange resin.

The oxidized Cu(II) ions are released from the anion-exchange resin and flow down through the Cu(I) adsorption band in the chromatographic column. During the passing down of the Cu(II) ions through the adsorption band, the isotopic electron-exchange reaction takes place between Cu(I) and Cu(II) ions

$$^{65}\underline{\text{Cu(I)}} + {}^{63}\text{Cu(II)} \rightleftharpoons {}^{63}\underline{\text{Cu(I)}} + {}^{65}\text{Cu(II)} \tag{10}$$

where the underlines represent the resin phase.

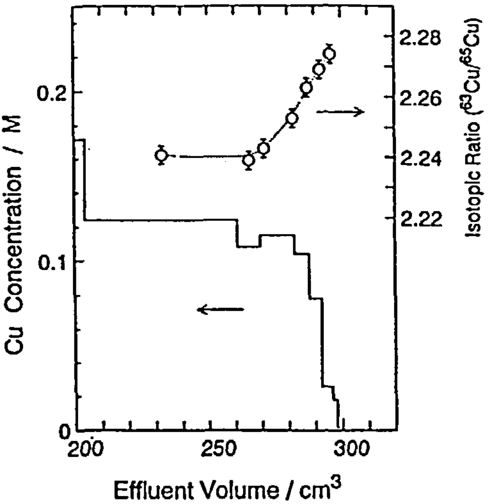

FIG. 4 Reverse breakthrough chromatogram and isotopic ratio curve of the Cu(I)/Cu(II) electron exchange system.

The observed concentrations and isotopic abundance ratios of copper in sample fractions are plotted in Fig. 4. Apparently $^{63}$Cu is enriched in the rear boundary region. The results clearly indicate that the lighter isotope of $^{63}$Cu is fractionated in the Cu(I) adsorbed in the resin phase. This means that the isotopic equilibrium constant of Eq. (10) is larger than unity or that the equilibrium of Eq. (10) shifts slightly to the right-hand side. From the rear part of the chromatogram in Fig. 4, the separation coefficient $\epsilon_r$ of the present electron-exchange system is calculated in the same way as previously described for LXS and is $3.8 \times 10^{-4}$. Because the chromatograph was made in the reverse breakthrough manner, a front boundary was not created. The observed $\epsilon_r$ is regarded as the separation coefficient $\epsilon_E$ of the present electron-exchange system (EXS).

The isotopic equilibrium constant $K$ is closely related to the experimentally obtained separation coefficient $\epsilon$ in any isotope-exchange system. In the ideal case where the two chemical species concerned are perfectly separated between two phases [in other words, all Cu(I) ions exist in the resin phase and all Cu(II) ions exists in the solution phase], the separation coefficient $\epsilon_E$ agrees with the theoretical isotopic equilibrium constant $K - 1$ or $\ln K$, which is expressed by $\epsilon_{EO}$. Then the following equation holds:

$$\epsilon_E \leq \epsilon_{EO} = \ln K \quad (11)$$

In actual cases, ions of both Cu(I) and Cu(II) partly exist in the counterphase for each ion. However, the extent of mixing is considered to be small, and the value of $\epsilon_E$ can be used as an approximation of the $\epsilon_{EO}$ value. In the same way, the previously obtained value of $\epsilon_L$, $2.8 \times 10^{-4}$, for LXS is assumed to be $\epsilon_{LO}$ or $K - 1$ of Eq. (2).

Since Cu(I) ions form complexes with ligands such as $Cl^-$ more strongly than do Cu(II) ions, Cu(I) ions were preliminary deduced to be enriched in the heavier isotope $^{65}Cu$ according to the general rule of the conventional theory for the isotope effects arising from molecular vibration. However, the experimental results are opposite to the prediction. In addition, the observed separation coefficient for $\epsilon_E$ of $3.8 \times 10^{-4}$ is larger than for $\epsilon_L$, $2.8 \times 10^{-4}$. It is interesting to consider the real reason for the isotopic effects in EXS. The state of Cu(II) ions in aqueous solutions in EXS is assumed to be practically equivalent to the state of Cu(II) ions in the cation-exchange resin in LXS, since the isotopic effects in a pure ion-exchange process without complex formation are known to be very small and frequently negligible. The order of the isotopic effects in the two systems, LXS and EXS, are combined and presented in Fig. 5, although the real reason for the isotopic effects in EXS has been not yet clarified. Figure 5 suggests that a larger separation coefficient, 6.6

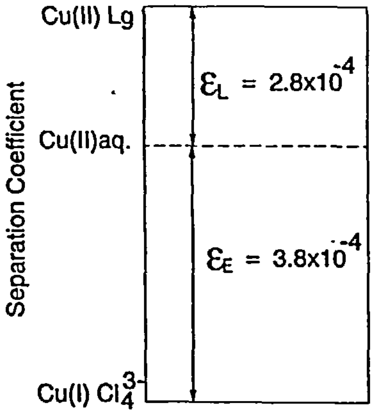

FIG. 5 Isotopic effects of Cu in the LXS and EXS. The symbol Cu(II) Lg represents the Cu–ligand complex phase, Cu(II) aq. the Cu(II) aqueous phase, and $Cu(I)Cl_4^{3-}$ the Cu(I) chloride complex phase. $\epsilon_L$ is the separation coefficient in the LXS and $\epsilon_E$ the separation coefficient in the EXS. Experimental conditions are given in Table 1.

$\times 10^{-4}$, may be obtained if the Cu(II) complex and the Cu(I) complex can coexist in the same system.

## CONCLUSIONS

1. The ideal displacement chromatogram in LXS was obtained using malic acid as a function of the complex-forming reagent in a relatively long migration. The heavier isotope $^{65}$Cu was clearly found to be enriched at the front boundary of the Cu adsorption band, and lighter isotope $^{63}$Cu was enriched at the rear boundary in the LXS.
2. A theoretical estimation method was developed to obtain the true value of $\epsilon$ from the system where isotopic remixing takes place in the central part of the migration band. On the basis of the theoretical estimation method, $\epsilon_L$ of the malic acid LXS has been calculated as $2.8 \times 10^{-4}$.
3. In the Cu(I)/Cu(II) EXS using an anion-exchange resin, the lighter isotope $^{63}$Cu was found to be enriched at the Cu(I) side and the heavier isotope $^{65}$Cu was enriched at the Cu(II) side. The observed separation coefficient was $3.8 \times 10^{-4}$ in the EXS.
4. Since Cu(II) malate and Cu(I)$Cl_4^{3-}$ are both in the strongly complexed form compared with Cu(II) aqueous ions, it is expected that both complex species will be enriched in the heavier isotope compared with aqueous Cu(II) ions. But the results show that Cu(II) malate is enriched in the heavier isotope while Cu(I)$Cl_4^{3-}$ is enriched in the lighter isotope. The separation coefficient $\epsilon_E$ of Cu(I)/Cu(II) EXS was observed to be $3.8 \times 10^{-4}$, which is larger than the $\epsilon_L$ of LXS obtained in the present work. The electron-exchange system may show isotope effects different from the ordinary isotope effects shown in complex formation systems.

## ACKNOWLEDGMENT

The present work was supported by the REIMEI Research Resources of Japan Atomic Energy Research Institute.

## REFERENCES

1. T. I. Taylor and H. C. Urey, *J. Chem. Phys.*, *6*, 429 (1938).
2. Z. Hagiwara and Y. Takakura, *J. Nucl. Sci. Technol.*, *6*, 326 (1969).
3. T. Oi, K. Kawada, M. Hosoe, and H. Kakihana, *Sep. Sci. Technol.*, *26*, 1353 (1991).
4. M. Aida, Y. Fujii, and M. Okamoto, *Ibid.*, *21*, 643 (1986).
5. K. A. Piez and H. Eagle, *J. Am. Chem. Soc.*, *78*, 5284 (1956).
6. F. H. Spedding, J. E. Powell, and H. J. Svec, *Ibid.*, *77*, 1393, 6125 (1955).
7. B. E. Jepson and G. C. Shockey, *Sep. Sci. Technol.*, *19*, 173 (1984); *22*, 1029 (1987).

8. N. Kobahashi, Y. Fujii, M. Okamoto, and H. Kakihana, *Bull. Res. Lab. Nucl. React.*, *5*, 19 (1980).
9. T. Oi. S. Yanase and H. Kakihana, *Sep. Sci. Technol.*, *22*, 2203 (1987).
10. T. Oi, H. Ogino, M. Hosoe, and H. Kakihana, *Ibid.*, *27*(5), 631 (1992).
11. K. Kogure. M. Nomura, and M. Okamoto., *J. Chromatogr.*, *259*, 480 (1983).
12. K. Kogure, M. Kakihana, M. Nomura, and M. Okamoto, *Ibid.*, *325*, 195 (1985).
13. Y. Fujii, J. Fukuda, and H. Kakihana, *J. Nucl. Sci. Technol.*, *15*(10), 745 (1978).
14. T. Kanzaki, Doctoral Thesis (in Japanese), Tokyo Institute of Technology, Japan, 1967.
15. Y. Fujii, M. Hosoe, and M. Okamoto, *Z. Naturforsch.*, *41a*, 769 (1986).
16. J. Bigelesen, *J. Am. Chem. Soc.*, *118*, 3676 (1996).
17. M. Nomura, N. Higuchi, and Y. Fujii, *Ibid.*, *118*, 9127 (1996).
18. H. Y. Kim, M. Kakihana, M. Aida, K. Kogure, M. Nomura, Y. Fujii, and M. Okamoto, *J. Chem. Phys.*, *81*(12), 6266 (1984).
19. F. H. Spedding, J. E. Powell, and H. J. Svec, *J. Am. Chem. Soc.*, *77*, 6125 (1955).
20. H. Kakihana and T. Kanzaki, *Bull. Tokyo Inst. Technol.*, *90*, 77 (1969).
21. Y. Fujii, M. Aida, and M. Okamoto, *Sep. Sci. Technol.*, *20*(5&6), 377 (1985).

*Received by editor May 2, 1997*
*Revision received September 1997*