Isotope Effects of Copper in Cu(II) Ligand-Exchange Systems by Ion Exchange Chromatography

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(Manuscript submitted September 3, 2001; in final form received December 25, 2001)

Abstract

The isotope effects of copper in ligand exchange processes were studied by means of chelating ion exchange resin system and EDTA complex/cation-exchange resin system. Two cases of different ionic interactions systems were investigated using chelating ion exchange resin system; Cu-H and Cu-Co systems. Both cases were investigated using the breakthrough technique, while the reverse breakthrough technique was applied in the case of EDTA. The chromatograms obtained from two different chelating resin systems were not ideal but they can be improved in future work. The heavier isotope $^{65}$Cu was found to be enriched in the ligand side in all cases, the resin phase in the case of chelating resin and the solution phase in the case of EDTA complex system. The separation coefficients in the two chelating systems were found to be constant and equal to $1.1 \times 10^{-5}$. Concerning the EDTA complex system, the chromatogram obtained was ideal one and the separation coefficient was found to be $1.3 \times 10^{-5}$.

1. Introduction

Many methods have been developed for the separation of isotopes utilizing slight differences in physical and/or chemical properties. Chemical exchange methods such as amalgam/aqueous1,2), amalgam/organic3), solvent extraction4) and ion exchange chromatography5-10) were successfully used to separate the isotopes of a variety of elements. Enrichment of isotopes by ion exchange chromatography has been developed gradually for several decades after the first report on chromatographic enrichment of metal isotopes in 19385). In the early fifties, highly enriched nitrogen isotopes were achieved by chromatography6). Recently, uranium redox displacement band chromatography has reached an advanced stage and is seriously considered for commercial market7). Thus, chromatography technique for isotope separation is steadily approaching practicality.

Ligand exchange chromatography is one of the chromatographic processes used for the isotope separation of europium8), gadolinium9), uranium10,11), lithium12), calcium13), copper14) etc. According to the complexation reaction involved, ligand exchange chromatography can be separated into three different systems:

1. A conventional cation-exchange resin containing sulfonate or carboxylate groups, which do not form complexes with cation, is used and the complexing agent is present as a solute in the liquid phase.
2. A conventional anion exchange resin containing tertiary amine or quaternary ammonium groups adsorbs anionic complexes of cations.
3. A chelating resin contains a chelating agent as functional groups fixed into its matrix, and the liquid phase does not contain a complexing agent.

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In a previous work\textsuperscript{14}, we have shown the copper isotope effects in the ligand exchange system by ion exchange chromatography using malate as a complexing agent added, as a solute, to the liquid phase. This accords with the first type of ligand exchange chromatography mentioned above. In the present work the first type ligand exchange chromatography, where EDTA is used as a ligand, and the third type, chelating resin, will be studied. These two systems have been chosen because the functional group of the available chelating resin CR–10 is similar to that of EDTA. Besides, both of them had been used for the separation of isotopes of many elements.

Chelating resins have been used recently for studying the isotope effects of a variety of elements. B. E. Jepson and W. F. Evans used different chelating resins for studying the isotope effects of Ca by means of breakthrough chromatography technique\textsuperscript{13}. T. Oi et al. used Diaion CRB02 and IRA743, both are chelating resins, for studying the isotope effects of boron\textsuperscript{15}. They found that the reverse break-through chromatography profile depends on pH value. Novel azacrown and monobenzo-15-crown-5 chelating resins were used successfully for the separation of lithium isotopes by D. W. Kim et al\textsuperscript{12,16}. EDTA was also used for the study of isotope separation of different elements such as europium\textsuperscript{8}, lead\textsuperscript{17}, gadolinium\textsuperscript{18}, etc.

The aim of this work is to study the copper isotope effects in EDTA complex exchange reaction and in the chelating resin exchange reaction.

2. Experimental

2.1 Ion Exchange Resin and Reagents

The ion-exchange resin used in the case of chelating ion exchanger system was a porous type chelate resin, CR–10, originally in the Na\textsuperscript{+} form, diameter 1190–297 μm, manufactured by Mitsubishi Chem. Ind. Ltd. The exchange capacity of the resin in the Na\textsuperscript{+} form was about 0.5 mmol Cu/ml resin at pH = 4.5. The CR–10 chelating resin is one of iminodiacetic acid type resins, styrene-divinylbenzene copolymer incorporating iminodiacetate group\textsuperscript{19}. This resin has a very high selectivity for divalent ions according to the following selectivity series:

\[
\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Na}^{+}
\]

In the case of EDTA complex exchange system, the resin used was highly acidic cation exchange resin. All other reagents used were of analytical grade and were used without further purification.

2.2 Chromatographic process

2.2.1 Chelating Exchange System

Two chromatographic experiments were carried out in the breakthrough manner. For each experiment, three chromatographic columns (100 cm in length × 8 mm inner diameter, made of pyrex glass, with water jacket) were connected in series with Teflon tube (1 mm in inner diameter). Then, they were used in a merry-go-round way, so that the total development length of the adsorption band was ~550 cm. In the first experiment, columns were conditioned with 2 M HCl, to remove the impurities and to convert the resin bed into H\textsuperscript{+} form. Thereafter, a feed solution of 0.05 M CuCl\textsubscript{2} was fed into the first column at a constant flow rate by a high pressure pump. When the copper adsorption band started to breakthrough from the last column, the effluent was portioned into fractions of 3 cm\textsuperscript{3}.

In the second experiment system, the columns were conditioned with 1 M aqueous NaOH, to remove the impurities and to convert the resin bed into Na\textsuperscript{+} form. Thereafter, CoCl\textsubscript{2} solution was poured into the resin bed to convert it into Co\textsuperscript{2+} form and then a 0.05 M CuCl\textsubscript{2} solution was fed into the first column at a similar flow rate. The effluents were collected from the last column and portioned into fractions. The temperature of the columns in both systems was kept constant at 80 ± 0.2°C throughout the experiments by passing temperature-controlled water through the water jackets of the columns. The experimental arrangement of the apparatus used in this work is similar to the arrangement shown previously\textsuperscript{8}.

2.2.2 EDTA Complex Exchange System

A copper isotope separation experiment based on the EDTA ligand exchange system was carried out using the same columns described above. These columns were packed uniformly with the strongly acidic cation exchange resin, TITECH–3, 37–88 μm. The resin was pretreated with 2 M HCl solution to remove the impurities and to be converted into the H\textsuperscript{+} form. Then, a 0.25 M CuNO\textsubscript{3} + 0.1 M HNO\textsubscript{3} solution was fed into the first column at a constant flow rate by a high pressure pump to convert the resin into Cu\textsuperscript{2+} ion form. The adsorption band of Cu\textsuperscript{2+} was visible, blue. Thereafter, Pb\textsuperscript{2+} adsorption band was formed by feeding Pb\textsuperscript{2+} solution into the first column after the formation of the Cu\textsuperscript{2+} ion band. To avoid shrinking of the resin at the band boundary when the ion form is changed, similar divalent cation, Pb\textsuperscript{2+}, was selected as the replacing ion for Cu\textsuperscript{2+} ion. When the Pb\textsuperscript{2+} adsorption band had grown to an appropriate length, the supply of the feed solution was stopped. Then both Pb\textsuperscript{2+} and Cu\textsuperscript{2+} ion were eluted by an eluent, 0.025 M NH\textsubscript{4}–EDTA solution adjusted to pH 8.21
Table 1 Experimental conditions and final results of the three runs

<table>
<thead>
<tr>
<th>System</th>
<th>Chelating resin (Cu-H)</th>
<th>Chelating resin (Cu-Co)</th>
<th>Cu-EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>CR-10 (1190-297 μm diameter)</td>
<td>CR-10 (1190-297 μm diameter)</td>
<td>Strongly acidic cation exchange resin (TITECH-2, 30-80 μm)</td>
</tr>
<tr>
<td>Feed solution</td>
<td>0.5 M CuCl₂</td>
<td>0.5 M CuCl₂</td>
<td>0.25 M CuNO₃ + 0.1 M HNO₃</td>
</tr>
<tr>
<td>Bed form</td>
<td>H⁺</td>
<td>Co²⁺</td>
<td>—</td>
</tr>
<tr>
<td>Migration length</td>
<td>5.5 m</td>
<td>5.5 m</td>
<td>42 m</td>
</tr>
<tr>
<td>Band velocity</td>
<td>3 cm/hr</td>
<td>2.8 cm/hr</td>
<td>5.8 cm/hr</td>
</tr>
<tr>
<td>Temperature</td>
<td>80.0 ± 0.2°C</td>
<td>80.0 ± 0.2°C</td>
<td>50°C ± 0.2°C</td>
</tr>
<tr>
<td>Separation Coefficient</td>
<td>1.1×10⁻⁴</td>
<td>1.1×10⁻⁵</td>
<td>1.3×10⁻⁵</td>
</tr>
<tr>
<td>HETP</td>
<td>0.056 cm</td>
<td>0.033 cm</td>
<td>0.12 cm</td>
</tr>
</tbody>
</table>

with a NH₄OH solution. The eluent was fed at the same flow rate as the feed solution. The three packed columns were repeatedly used in a merry-go-round way. After the Cu²⁺ ion adsorption band was eluted out from the last columns, the effluents were collected in small fractions and were subjected to the concentration analysis and the isotopic analysis. The temperature of the columns was kept constant at 50.0 ± 0.2°C by circulating the thermostatted water through the water jackets surrounding the columns. The apparatus used for the separation of copper isotopes is similar to that schematically shown before. The experimental conditions and results are summarized in Table 1.

2.3 Analysis

Concentration of copper samples was measured by inductively-coupled-plasma atomic emission spectrometry (ICP-AES) Model SPS 1500VR, Seiko Instruments, at the wavelength 381.967 nm after appropriate dilution with 0.1 M HCl. For the feed solution and some selected fractions of the effluent of each experiment, the ⁶³Cu/⁶⁵Cu isotopic ratios were measured by a MAT 261 mass spectrometer with a thermal ionization method. Operational technique details of mass spectrometer has been discussed in a previous work. The error of the copper isotopic ratio measurement is usually 0.1-0.2%.

Prior to the mass spectrometric isotope analysis, the samples containing some amount of cobalt ions were subjected to purification. In this concern, 3 M HCl was added to the sample and then the solution was fed to a small column packed with anion exchange resin. Cu²⁺ ions were sorbed by the resin while Co²⁺ ions were not. Then, the Cu²⁺ ions were eluted with distilled water and converted to copper nitrate for mass analysis.

3. Results and Discussion

3.1 Chelating Exchange System

Due to the higher selectivity of CR-10 to Cu²⁺ ions over that of H⁺ or Co²⁺ ions as was shown before, Cu(II) is sorbed by the resin when it reaches the rear boundary of H⁺ ion band, in case of Cu-H system, and of Co, in Cu-Co system, adsorption bands forming a growing Cu(II) band. Another reason for the selection of H⁺ ion and Co²⁺ ion as the preceding ion is the prevention of resin shrinking when the Cu²⁺ ion band is formed. In this respect, NH₄⁺ ion, for example, is not appropriate, because the resin shrinks when converted to Cu²⁺ type and the boundary is likely to tilt. During the passing down of the fed Cu²⁺ ions through the copper adsorption band, the isotopic ligand exchange reaction takes place between Cu²⁺ ions in the solution phase and Cu(II) chelate complex in the resin phase as given by eq. (1)

\[ R^{63}\text{Cu} + 65\text{Cu}^{2+} \rightleftharpoons R^{65}\text{Cu} + 63\text{Cu}^{2+} \] (1)

where R represents the resin. The chromatograms obtained in both Cu-H system and Cu-Co system were almost the same. Fig. 1 shows the concentration profile and the isotope abundance ratios of the Cu-H system. In both systems the breakthroughs were not sharp and chromatograms were not ideal. This could be due to the slow ion exchange reaction in the case of chelating resins compared to the normal cation or anion exchange resins. A similar performance was found in the case of calcium isotope effects studied by chelating exchange chromatography. It is usually possible to improve the ion exchange performance by changing the band velocity. For any chromatographic process there is an optimum band velocity at which the boundary is sharp and a height equivalent to a theoretical plate, HETP, is minimum.

In both systems, the light isotope, ⁶³Cu, has been observed to be enriched at the front boundary region of the copper adsorption band, which means that the isotopic equilibrium constant of eq. (1) is larger than unity.

The single stage separation factor, \( \alpha = 1 + e \), for the ⁶³Cu isotope.
The Cu$^{65}$Cu isotopic pair is defined here as:

$$\alpha = \frac{[\text{Cu}] / [\text{Cu}^+] / [\text{Cu}^+] / [\text{Cu}^+]}{[\text{Cu}^+] / [\text{Cu}^+]} \quad (2)$$

The net isotope effect term $\alpha$, which is referred as the isotope separation coefficient, is calculated using the equation developed by Spedding$^6$ and Kakihana$^{21}$ as described in a previous work$^{22}$. The value of $\alpha$ was found to be constant in both cases and equal to $1.1 \times 10^{-5}$. This revealed that the isotope exchange reaction is the same in both cases. In fact, the replacement of H$^+$ by Co$^{2+}$ was carried out to reduce the resin shrinkage effect. In the case of H$^+$ form, the resin bed height highly changed during the adsorption/regeneration cycles, which is troublesome during the chromatographic process. The separation coefficient would only be largely changed if the structure of Cu$^{2+}$ ion species in the solution or in the resin phase had largely been changed. This was the case of boron as mentioned by T. Oi et al.$^{15}$.

The observed separation coefficient of Cu$^{2+}$ chelating resin system is considered very small compared to the previously shown data in case of copper-malate ligand exchange chromatography and Cu(I)—Cu(II) electron exchange chromatography$^{22}$. These low values could be due to the high temperature we had to use to improve the chelating reaction kinetics. If lower temperature was used, the chelating exchange reaction would be sluggish and the boundaries of the chromatogram would be much more broadened. In such cases the separation coefficients cannot be determined.

### 3.2 EDTA Complex Exchange System

The ion exchange reaction involved in the EDTA complex exchange system first takes place at the interface between the Pb$^{2+}$ and Cu$^{2+}$ adsorption bands. When the Pb$^{2+}$ complexes reached the rear boundary of the Cu$^{2+}$ adsorption band, the ligand species are transferred from Pb$^{2+}$ to Cu$^{2+}$ ions because of the large stability constant for the Cu-EDTA ligand complex formation (eq. 3). 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 phase (eq. 4).

$$\text{PbLg} + \text{Cu}^{2+} \rightarrow \text{Pb}^{2+} + \text{CuLg} \quad (3)$$
$$^{65}\text{Cu}^{2+} + ^{63}\text{CuLg} \rightarrow ^{63}\text{Cu}^{2+} + ^{65}\text{CuLg} \quad (4)$$

where Lg indicates ligand and the underlines represent the species in the resin phase. The chromatogram of copper in the EDTA ligand exchange system after a migration of 42 m and the isotope abundance ratios observed in the displaced band are shown in Fig. 2, which is almost ideal one.

The dotted line shows the isotopic abundance ratio in the feed solution. It is clearly seen that the heavier isotope, $^{65}$Cu, is depleted at the boundary of the reverse breakthrough chromatogram. This means that the heavier isotope was enriched in the solution phase, complex form. Comparing this finding with the two cases of chelating ion exchanger chromatography described above and the case of copper malate described previously$^{14,22}$, it is clear that in all cases the heavier isotope $^{65}$Cu was enriched in the
complex formation side; the solution phase, if it contains malate or EDTA complexing agent as a solute, or in the resin side, if the resin contains the chelating agent. These experimental findings agree with the molecular vibrations isotope effects theory established by Bigeleisen and Mayer\(^{23}\). According to this theory, the equilibrium constant is calculated as the difference between the reduced partition function ratios, \((s/s')_\text{f}^T\), of two different isotopic chemical species. The theory leads to the prediction that the heavy isotope is to be enriched in the strongly complexed form side. This tendency is also the same as that observed in the chromatographic isotope separation of many elements such as europium\(^{8}\), uranium (IV)\(^{24}\), calcium\(^{13}\) etc.

The separation coefficient \(\epsilon\) of Cu-EDTA system in the present work was calculated from the experimentally observed isotopic enrichment curve of the chromatogram and was found to be \(1.3 \times 10^{-5}\).

Fig. 3 shows a schematic, not to scale, presentation of the \(\epsilon's\) of Cu-malate exchange system, Cu-EDTA exchange systems and Cu(I)–Cu(II) electron exchange system at 323 K. The value of Cu-CR-10 exchange system was reported at a higher temperature, 353 K, but we believe that its value at the same temperature will be slightly higher within the same order. From this figure, it is clear that the value of Cu-EDTA separation coefficient is very small compared to that of Cu-malate system. EDTA was expected to have more strong coordination bonds with copper than malate. Thus, according to the molecular vibration theory, the copper isotope effects in case of EDTA ligand exchange system were expected to be larger than the copper isotope effects in the case of malate ligand exchange system, similar to the case of Gd-EDTA system which has larger separation coefficient compared to Gd-malate system\(^{17}\). It is so difficult to explain this contradictory between the copper case and the gadolinium case according to the available knowledge. The Cu-EDTA complex may have, due to unknown reasons, weaker coordination bonds than the Cu-malate.

The field shifts effect may be also one of the reasons to be considered. According to the new theory of the field shifts effect on the isotope effects\(^{25}\), the field shifts are proportional to the change in the electron density at the nucleus. As the heavier isotope has a larger volume and smaller charge density of the nucleus, it will be enriched in the species with the lowest electron density at the nucleus. In the case of copper EDTA complex, the electron density at the copper nucleus is expected to be higher than the case of copper malate complex due to the coordination of, the electron donor, nitrogen atom to the copper atom in the EDTA complex. In copper EDTA ligand exchange system, two opposite factors may be affecting copper isotope effects, molecular vibrations which enrich the heavier isotope \(^{65}\text{Cu}\) in EDTA complex side and the field shifts which would enrich the lighter isotope \(^{63}\text{Cu}\) in EDTA complex side. In such case, the observed isotope effects would be the net resultant of these two factors taking into account that the molecular vibration effects are the major factor as the heavier isotope was found to be enriched in the EDTA complex side. This conclusion agrees with the conclusions reached during the study of temperature effect on the copper isotope effects by Cu(I)–Cu(II) electron exchange system\(^{26}\) and Cu-malate ligand exchange system\(^{14}\).

4. Conclusions

The isotope effects of copper were studied by means of chelating ion exchange chromatography and EDTA ligand exchange chromatography. Two different ionic interaction cases were investigated in the case of chelating systems with the ion form of Cu–H and Cu–Co using breakthrough technique. In the case of EDTA system, the chromatogram obtained was ideal one. The separation coefficient in the two chelating systems was found to be constant and equal to \(1.1 \times 10^{-5}\). In the case of EDTA ligand exchange chromatography, the separation coefficient was found to be \(1.3 \times 10^{-5}\).

References

イオン交換クロマトグラフィーによる銅（II）配位子交換系における銅の同位体効果

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（受付日：2001年9月3日，受理日：2001年12月25日）

配位子交換過程における銅の同位体効果を、キレート樹脂法とEDTA酸化系のクロマトグラフィーによって研究した。キレート樹脂系では二つの異なるイオン相互作用のケース（Cu-H系とCu-Co系）で実験を行った。この二つの場合にはブレーキルル方式で実験され、EDTA系の場合は濃縮ブレーキルル方式で行われた。全ての場合において同位体異性体の146Cuが有機配位子を持った樹脂の方に濃縮した（キレート樹脂系においては樹脂相、EDTA酸化系においては溶解相）。キレート樹脂系の場合の同位体分離係数εは1.1×10^{-5}であり、EDTA系においては理論的なクロマトグラムが得られ、同位体分離係数εは1.3×10^{-5}であった。