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Temperature Effect on Copper Isotopes Separation by Electron-Exchange Reaction Using Anion-Exchange Chromatography

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ABSTRACT

Anion-exchange chromatography of copper has been carried out to study copper isotope separation based on the Cu(I)/Cu(II) electron-exchange reaction at various temperatures. At every temperature the lighter isotope, ^{63}Cu, was observed to be enriched at the rear part of the copper adsorption band. The results indicate that the lighter isotope is preferentially fractionated into Cu(I) ions in the resin phase. Single-stage separation coefficients, ε (= $\alpha - 1$), were calculated for the ^{63}Cu /^{65}Cu isotopic pair at different temperatures. The results show that the separation coefficient ε obtained is decreased by increasing the temperature. The height equivalent of a theoretical plate (HETP) was determined in every experiment and found to be almost constant at different temperatures.

INTRODUCTION

Naturally occurring copper consists of two isotopes: ^{63}Cu (69.17%) and ^{65}Cu (30.83%). Copper isotopes are interesting materials for electronic device, and in addition they are used in research on life science as stable isotope tracers since copper is a very important element in plants (1, 2) and animals (3, 4). So far stable copper isotopes have been produced by the electromagnetic method which is an energy consuming and costly process.

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On the other hand, chemical exchange isotope separation is less energy consuming and appropriate for large-scale production. Most light element isotopes have been produced by the chemical exchange method, but the production of stable isotopes of heavy elements by chemical exchange has been regarded as unfeasible because of the small isotopic separation coefficients. Relatively large isotope effects have been found recently in chemical exchange systems involving different valence states of the isotopes concerned. This has placed renewed attention on the copper isotope effects in electron-exchange chemical reaction systems.

The ion-exchange process is an efficient medium for the multiplication of small isotope effects. However, research has been very limited in the field of copper isotope separation by ion exchange. Copper isotope effects in electron migration were studied by using cation exchange (5). In our previous work the Cu(II) malate ligand-exchange system (LXS) and the Cu(I)/Cu(II) electron-exchange system (EXS) were studied, and EXS showed a larger isotope separation coefficient than did LXS (6).

In order to find appropriate conditions for copper isotope separation, the temperature dependence of isotope separation coefficients in the Cu(I)/Cu(II) electron-exchange system is studied in the present work by using anion-exchange chromatography. The temperature dependence of the separation coefficient is also interesting from the viewpoint of basic research on the isotope effects of electronic states.

EXPERIMENTAL

Materials

The ion-exchange resin used was a highly porous, strongly basic anion-exchange resin (AR01, 30–60 μm diameter) produced by Asahi Chemical Industries. All reagents used were of analytical grade and were employed without further purification.

Chromatographic Method

Copper isotope separation experiments based on EXS at four different temperatures were carried out with a displacement chromatography system. Two glass columns (0.8 cm I.D. × 100 cm length, with water jackets) were connected in series with a tetrafluoroethylene–perfluoroalkyl vinyl ether copolymer (TPEA PFA) tube (1 mm I.D.). The columns were packed uniformly with the strongly basic anion-exchange resin. The resin was pretreated with HCl solutions to remove impurities and convert it into the Cl^- form. Then a Cu(I) chloro-complex solution (0.2 M CuCl in 3 M HCl) was fed into the columns until all the resin was converted to the Cu(I) form. This Cu(I) adsorption band

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was eluted with ferric chloride solution (0.2 M $FeCl_3$ in 3 M HCl) at the same flow rate as the one used for the feed solution. When the Cu(I) adsorption band was eluted from the last column, the effluent was collected into small fractions and the fractions were subjected to concentration and isotopic analysis. A schematic diagram of experimental apparatus is shown as Fig. 1. The temperatures of the columns in the experiments were kept constant at 293.0 ± 0.2 K, 313.0 ± 0.2 K, and 353.0 ± 0.2 K by circulating thermostated water through water jackets surrounding the columns.

Analysis

The copper concentration in each fraction of the effluent was determined by using an inductively coupled plasma atomic emission spectrometry (ICP-

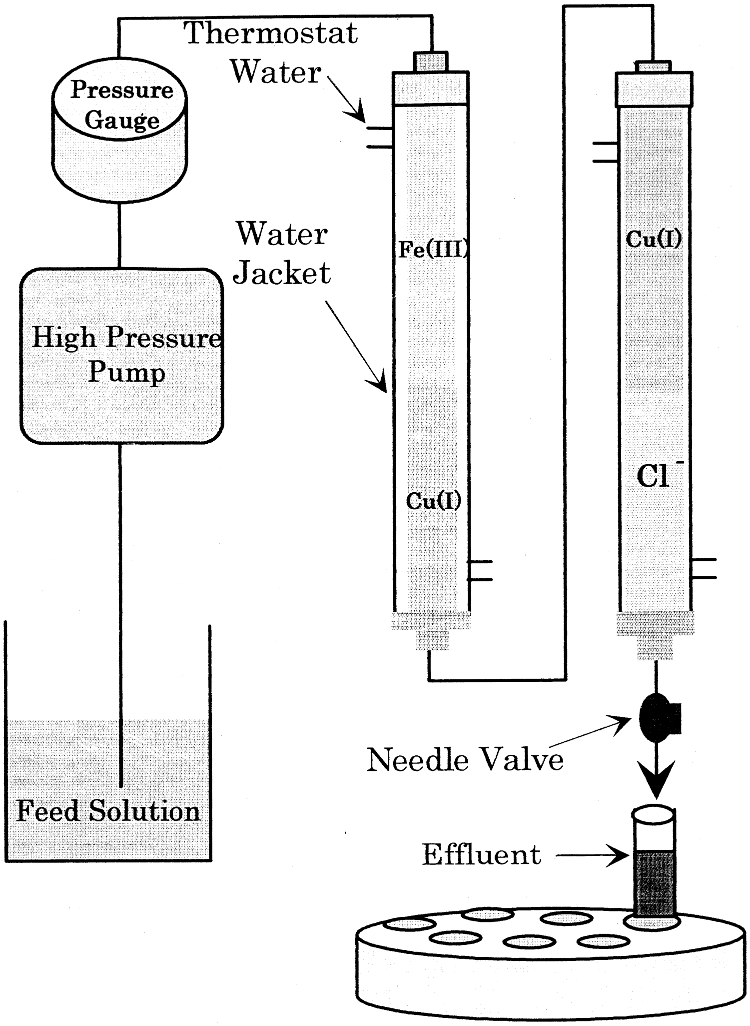

FIG. 1 Schematic of the redox chromatography column system used for the study of the electron-exchange Cu isotope effects.

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AES) system (Model SPS 1500VR, Seiko Instruments) at a wavelength of 381.97 nm after appropriate dilution with 0.1 M HCl. The $^{63}Cu/^{65}Cu$ isotopic ratios of copper samples were determined by using a Finnigan MAT 261 mass spectrometer with a thermal ionization method. The filament unit for sample ionization was comprised of two filaments made of rhenium ribbon, one for sample vaporization and the other for ionization. A drop (20 μg) of copper sample was loaded on the surface of the vaporizing filament and dried by heating with an electric current. Then the sample filament unit was inserted into the ion source of the mass spectrometer. Operational details of the mass spectrometry were described in previous papers (6, 7). The error of the copper isotopic ratio measurement was usually 0.1–0.2%.

RESULTS AND DISCUSSION

The experimental conditions are summarized in Table 1. The observed copper elution chromatograms and the profile of the $^{63}Cu/^{65}Cu$ isotopic ratios at the rear boundaries are plotted in Figs. 2–4. Apparently the lighter isotope, ^{63}Cu, is enriched at the rear boundary.

The standard electrode potentials of Cu(I)/Cu(II) and Fe(II)/Fe(III) are 0.153 and 0.771 V, respectively, at 298 K. These values indicate that the following oxidation–reduction reaction takes place when Cu(I) is contacted with Fe(III) ions:

$$\mathrm{Cu(I)} + \mathrm{Fe(III)} \rightarrow \mathrm{Cu(II)} + \mathrm{Fe(II)} \qquad (1)$$

The selectivities or the distribution coefficients of these ions in HCl solution have been reported by Kraus et al. (8) on quaternary ammonium ion type strongly basic anion exchange resins at room temperature. The distribution coefficients of Cu(I) and Fe(III) in 3 M HCl are very large of the or-

TABLE 1
Experimental Conditions of the Cu(I)/Cu(II) Redox Chromatography

Resin	Strongly basix anion-exchange resin (AR01, 30–60 μm)
Column	0.8 cm I.D. and 100 cm length
Temperatures (K)	293, 313, 353
Feed solution	0.2 M CuCl in 3 M HCl[a]
Eluent	0.2 M $FeCl_3$ in 3 M HCl
Flow rate	0.14 cm^3/min
Band velocity	0.08 cm/min

[a] A few milliliters of 0.2 M $TiCl_3$ in 3 M HCl was added to the feed solution to completely reduce any Cu(II) impurity in the solution.

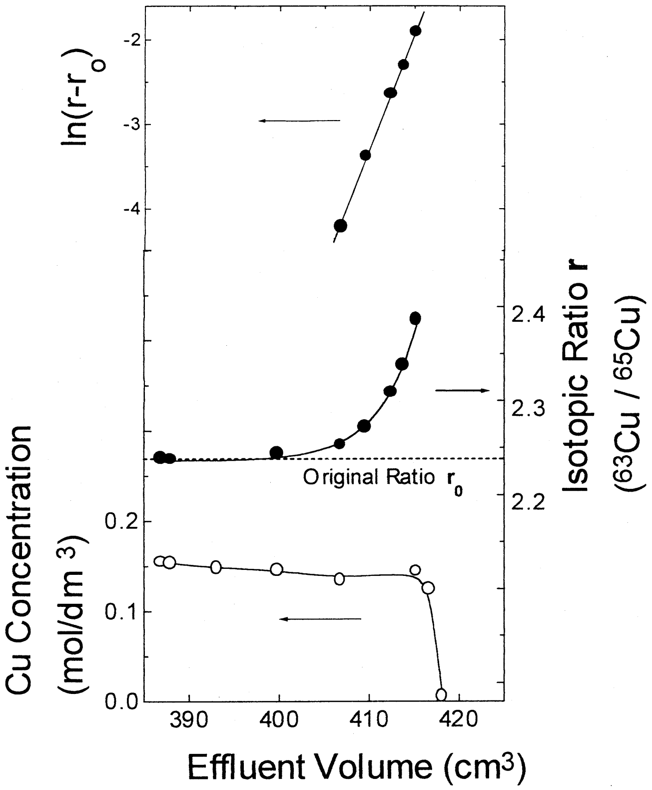

FIG. 2 Chromatogram and isotopic ratios of the Cu(I)/Cu(II) electron-exchange system at 293 K.

der of 10^2) and those of Cu(II) and Fe(II) are very small (these ions are practically not adsorbed).

Thus, in chromatographic operations the feed Fe(III) ions oxidize the Cu(I) ions initially adsorbed in the anion-exchange resin, then a Fe(III) band is formed, replacing Cu(I), and the oxidized Cu(II) ions are eluted from the resin:

$$2\mathrm{Fe(III)} + \mathrm{Cu(I)—R} \rightarrow \mathrm{Fe(II)} + \mathrm{Cu(II)} + \mathrm{Fe(III)—R} \qquad (2)$$

where —R represents the resin phase. It should be noted that the stoichiometric relation between the adsorbed Cu(I) and the fed Fe(III) in Eq. (2) is affected by the adsorbability of Fe(III) ions on the anion-exchange resin. Equation (2) should be regarded as a simplified model of the chemical reaction at the boundary.

During the passage of Cu(II) ions through the Cu(I) adsorption band, an isotopic exchange reaction repeatedly takes place between the resin phase and the solution phase:

$$^{63}\mathrm{Cu(II)} + {}^{65}\mathrm{Cu(I)—R} \rightleftharpoons {}^{65}\mathrm{Cu(II)} + {}^{63}\mathrm{Cu(I)—R} \qquad (3)$$

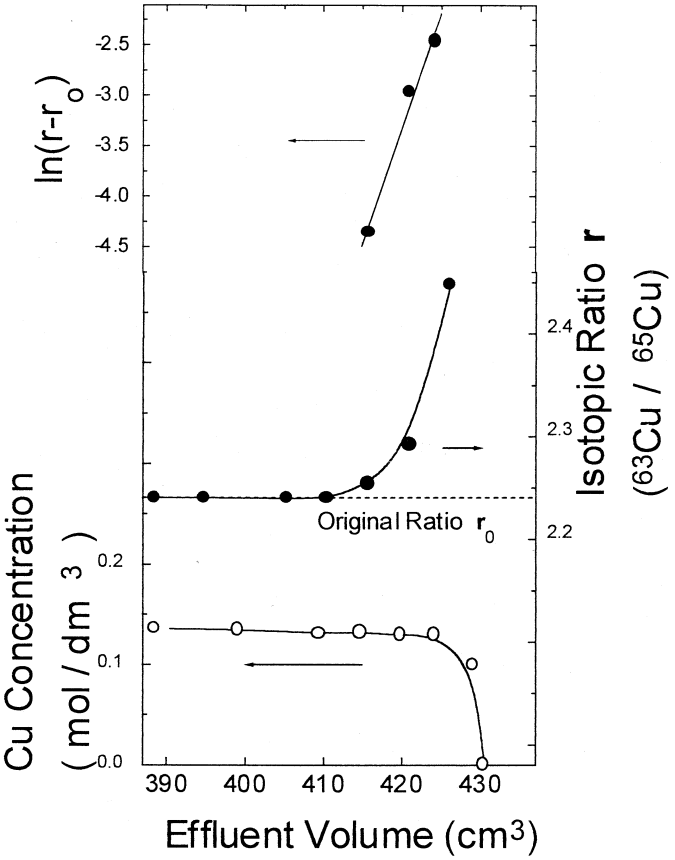

FIG. 3 Chromatogram and isotopic ratios of the Cu(I)/Cu(II) electron-exchange system at 313 K.

During the course of the chromatographic operation, one isotope is enriched at the rear boundary. The results presented in Figs. 2–4 indicate that the isotopic exchange equilibrium between two phases, as expressed by Eq. (3), is slightly shifted to the right-hand side.

The separation factor in the present work is defined as

$$\alpha = 1 + \varepsilon = \left[\frac{^{63}\mathrm{Cu}}{^{65}\mathrm{Cu}}\right]_{\mathrm{R}} \Big/ \left[\frac{^{63}\mathrm{Cu}}{^{65}\mathrm{Cu}}\right]_{\mathrm{S}} \qquad (4)$$

where ε is a separation coefficient (distinguished from the separation factor α) and suffixes R and S represent the resin and solution phases, respectively. Based on the experimentally observed eluent concentrations and isotopic ratios, values of ε were calculated for all the experimental runs at different temperatures. The calculation procedure was mentioned in a previous paper (6). The values of ε obtained at different temperatures are listed in Table 2 and plotted in Fig. 5.

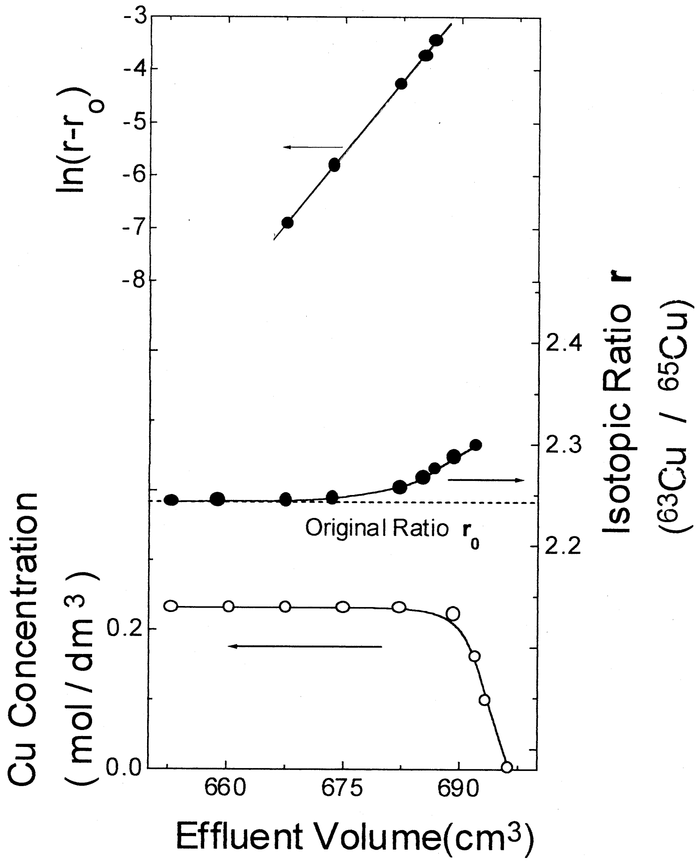

FIG. 4 Chromatogram and isotopic ratios of the Cu(I)/Cu(II) electron-exchange system at 353 K.

Cu isotope effects were studied in previous work (6) on the EDTA complex formation (or EDTA ligand-exchange) system at 323 K and the redox (or electron-exchange) system of Cu(I) and Cu(II) at 333 K. The ligand-exchange system has shown that ^{65}Cu rather than aqueous Cu(II) free ions is enriched in the EDTA complex species, the value of ε obtained for the system was 1.45 ×

TABLE 2
Experimental Results of Cu(I)/Cu(II) Redox Chromatography

Temperature (K)	Migration length (cm)	Separation coefficient, $\varepsilon \times 10^4$	HETP (mm)	Absorption capacity, Q (mmol/m)	Remarks
293	300	7.3	0.28	23	This work
313	300	6.5	0.34	23	This work
333	200	3.8	0.36	—	Previous work
353	500	2.2	0.33	40	This work

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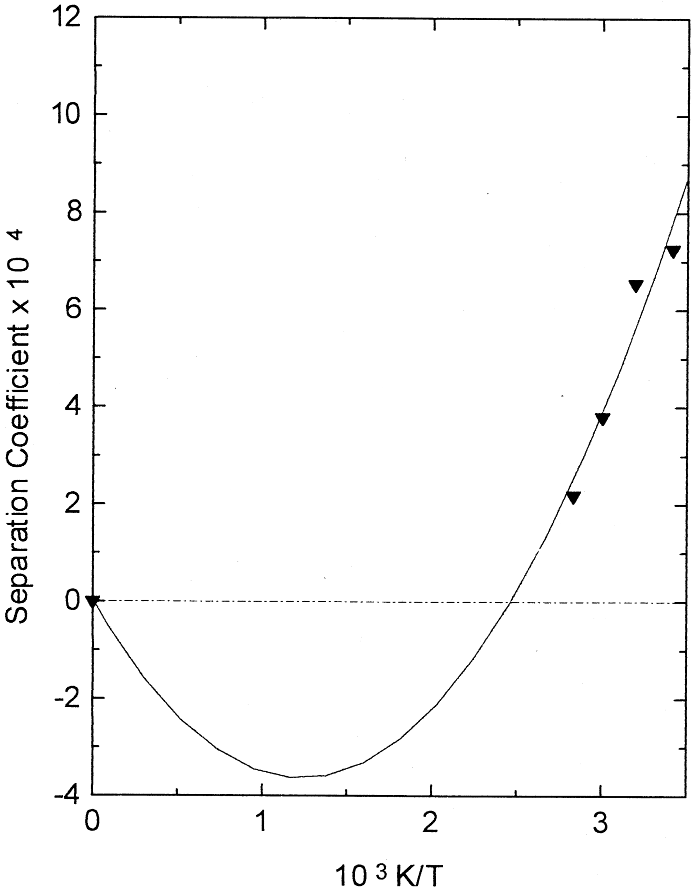

FIG. 5 Experimentally observed isotope separation coefficients of the Cu(I)/Cu(II) electron-exchange system.

10^{-4} at 323 K. On the other hand, ε of the electron-exchange system was determined to be 3.8×10^{-4}, where ^{63}Cu is preferentially enriched in the Cu(I) state. The present results on the enrichment tendency agree with the results for the Cu(J)/Cu(II) exchange system in the previous work. The previous values of ε obtained for the Cu(I)/Cu(II) exchange system are also presented in Table 2 and Fig. 5.

The plotted data in Fig. 5 were fitted to the following equation:

$$\varepsilon = A/T + B/T^2$$

which indicates the temperature dependence of the isotope equilibrium constant of heavy elements in electron-exchange systems (9, 10). Thus, the following equation shows the empirical temperature dependence of the separation coefficient of the Cu(I)/Cu(II) exchange system:

$$\varepsilon = -0.590/T + 239.8/T^2 \tag{5}$$

According to isotopic effects based on molecular vibration, the heavy isotope is expected to be fractionated into the strongly complexed species; here Cu(I) is more strongly complexed with Cl^- ions than Cu(II) in HCl solutions, as indicated by the fact that Cu(I) chloro-complexes are adsorbed in the anion-exchange resin. Therefore, it was expected that the lighter ^{63}Cu would be enriched in Cu(II) in the solution phase, but the experimental results are the opposite of that expectation.

The ε's of the ligand-exchange system of Cu(II) and the electron-exchange system of Cu(I)/Cu(II) are schematically presented in Fig. 6 by using the values of ε at 323 K, where the ε values of the Cu(I)/Cu(II) exchange system at 323 K are obtained as the average of the data at 313 and 333 K in Table 2. The general rule that the heavy isotope is enriched in the complex state is applicable to the Cu(II) ligand-exchange system. Based on this fact, the rule is estimated to be applicable to the ligand exchange of $Cu(I)_{complex}/Cu(I)_{aq.}$ system. However, that rule is not found to be applicable to the $Cu(I)_{complex}/Cu(II)_{eq.}$ electron-exchange system in the present work. The electron configurations of Cu(I) and Cu(II) may contribute to the isotope effects, but the real reason is not specified in the present work. Further studies are needed to elucidate the mechanism of the isotope effects in Cu(I)/Cu(II) exchange.

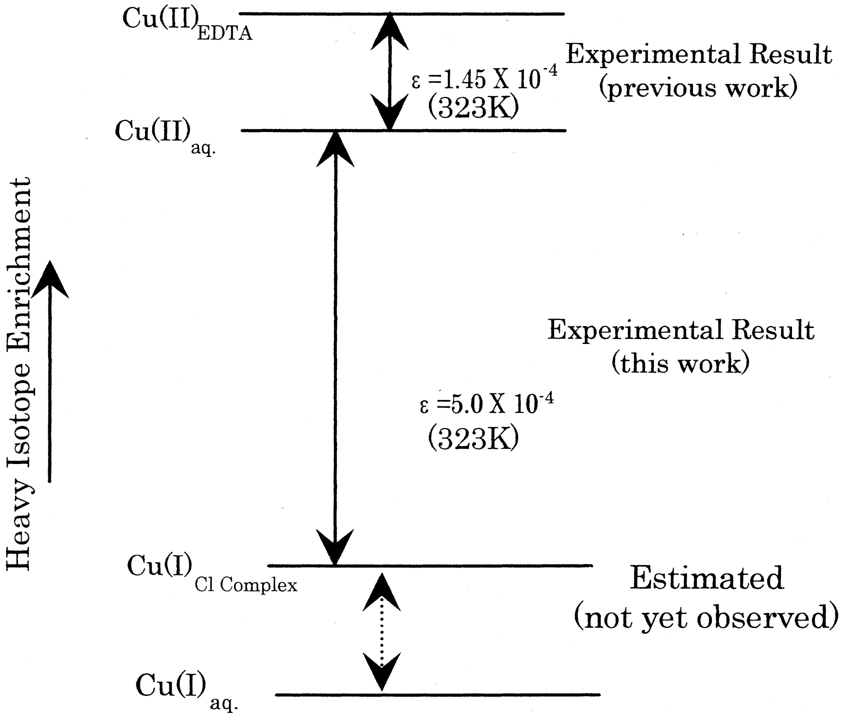

FIG. 6 Copper isotope effects of ligand-exchange and electron-exchange systems. ε of the Cu(I)/Cu(II) exchange system at 323 K is taken as the average between ε at 313 K and ε at 333 K.

The deviations in $\ln(r_i - r_o)$ of the isotopic ratio in each fraction (r_i) from the original value (r_o) are also plotted in Figs. 2–4. The slopes of the plots relate to the HETP (height equivalent to the theoretical plate) as expressed by the following equation (11):

$$\mathrm{HETP} = \frac{\varepsilon}{\theta} + \frac{1}{\theta^2 L} \tag{6}$$

where θ is the slope of the plots and L is the total migration length of the adsorption band boundary. The value of θ is calculated by

$$\ln(r_i - r_o) = \theta(X_i - L) \tag{7}$$

where r_i is the copper isotopic ratio of $^{63}\mathrm{Cu}/^{65}\mathrm{Cu}$ in the ith fraction, r_o is the copper isotopic ratio of the feed solution, X_i is the hypothetical distance of the sampled fraction, calculated from the starting point at the time when the boundary is eluted from the column after a migration distance of L. The hypothetical distance is calculated based on the effluent volume being proportional to the migration distance of the adsorbed band:

$$X_i = V_i / q_\mathrm{v}$$

where V_i is the effluent volume of the sample fraction i, and q_v is the effluent volume needed per 1 cm displacement of the band.

The determined HETPs are also listed in Table 2. The observed HETPs in the present work are very small compared to those reported in previous works on boron isotope separation using an anion-exchange resin (11); HETP = 1.8 mm. The results in the present work also indicate that the HETP values are quite small even at lower temperatures (293–313 K), and it is suggested that the isotope-exchange reaction rate of Eq. (3) is sufficiently large. The rate-determining step of Eq. (3) may be in the phase transfer process between the ion-exchange resin and the aqueous solution.

CONCLUSIONS

The temperature dependence of copper isotope effects in the Cu(I)/Cu(II) electron-exchange system was studied by redox ion-exchange chromatography using highly porous, strongly basic anion-exchange resin. The isotope separation coefficients, ε and HETP, were determined by reverse-breakthrough chromatographic operation at temperatures of 293, 313, and 353 K. The results clearly indicate that the lighter isotope (^{63}Cu) is enriched in Cu(I), which is in the form of a chloride complex anion adsorbed in the anion-exchange resin.

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