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ISOTOPE EFFECTS OF COPPER IN Cu(II) MALATE LIGAND EXCHANGE SYSTEM STUDIED BY USING ION EXCHANGE DISPLACEMENT CHROMATOGRAPHY

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ABSTRACT

The ion exchange chromatography technique was used for studying copper isotope effects in Cu-malate ligand exchange system (LXS) in the temperature range 288–353K. A highly acidic cation exchange resin (TITECH-3, 37–88 μm) was used. It had been found that the heavier isotope, ^{65}Cu, was enriched at the front boundary, while the lighter isotope, ^{63}Cu, was enriched at the rear boundary of the copper band at all temperatures. Such finding means that the heavier isotope, ^{65}Cu, is preferentially fractionated into the malic complex form in the solution phase. The values of the single stage separation coefficients, $\varepsilon = S - 1$, of the ^{63}Cu/^{65}Cu isotopic pair have been calculated and found to

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decrease with the increase in temperature as 2.87×10^{-4}, 2.39×10^{-4}, and 2.13×10^{-4} at 288, 333, and 353K, respectively. The height equivalent to the theoretical plate (HETP), at every temperature, was also calculated.

INTRODUCTION

The fact that elements in nature are mostly made up of various isotopes, each of them present in more or less abundance, is due primarily to the stability level of the individual nuclides and to the process of formation of these nuclides, either in the prestellar stages of the universe or in the interior of the stars. The interest in a research study on the separation of isotopes originally started as a scientific curiosity. Since the question that arose as to whether it was indeed feasible or possible to separate the isotopes of different elements was affirmatively answered, the isotopes of many elements were separated by different methods. The successful work of Urey paved the way for the evolution of an entirely new industry devoted to the separation of the isotopes of elements ranging from hydrogen to uranium (1). The needs of the isotopically labeled compounds have been now extensively increased. Enriched stable isotopes of many elements have been widely used in agriculture, pharmacology, medicine, biochemistry, and nuclear industry.

Many successful methods have been developed for the separation of isotopes utilizing slight differences in physical or chemical properties. The chemical exchange methods, in particular, were found to be adequate for the separation of many elements such as lithium (2,3), boron (4), carbon (5), nitrogen (6), calcium (7,8), magnesium (9), strontium (10), zirconium (11,12), europium (13,14), uranium (15), etc. In a previous paper, the possibility of separating copper isotopes by electron exchange system (EXS) and ligand exchange system (LXS) by means of ion exchange chromatography was studied (16). As the isotopic exchange reactions are still chemical reactions, having their rate of reactions and equilibrium constants, it is expected that temperature will highly affect the isotope separation by chemical methods. According to the molecular vibration theory, the increase in temperature will decrease the isotopic equilibrium constant as the equilibrium constant is inversely proportional to the square of the absolute temperature. This trend was experimentally found in the case of lithium (17), rubidium (18), copper (19), boron (20), uranium(IV)-malate, citrate, and lactate isotope effects systems (21). An opposite trend was observed in the case of barium (22), europium (14), and uranium (23) where the increase in temperature was found to increase the equilibrium constant of the isotopic exchange reaction. This was believed to be due to the mixing of volume effect and molecular vibrations (14,24). In such cases, the equilibrium constant is related to the temperature according to

$$K = (a/T) + (b/T^2) \qquad (1)$$

Hence, it is of interest to investigate the temperature effect on the isotope effects of the copper as one of the transient metals. The isotope effects of copper have been studied before by one of the present authors, Fujii et al. (24), by means of electromigration through a cation-exchange membrane, and by Abdul Matin et al. (16), by means of ion exchange chromatography. But in both cases the effect of temperature was not investigated.

Therefore, the aim of this work is to study the effect of temperature on the isotope effects of copper in copper malate exchange system using ion exchange displacement chromatography.

EXPERIMENTAL

Ion Exchange Resin and Reagents

The ion exchange resin used in the LXS was a highly porous, high cross-linked (20%), strongly acidic cation exchange resin (TITECH-3, 37–88 μm). The exchange resin was supplied by Asahi Kasei Corporation, Tokyo, Japan. All other reagents used were of analytical grade and were employed without further purification.

Chromatographic Processes

The chromatographic processes were carried out with a cyclic displacement chromatography system composed of three high pressure glass columns (0.8 cm inner diameter × 100 cm length, with water jackets), which were connected in series with teflon tubes (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 to be 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+} adsorbed band of an appropriate length (20–25 cm). The Cu^{2+} adsorbed band was eluted by an eluent, ammonium malate solution adjusted by NH_4OH solution to pH 5.5. The adsorbed band of Cu^{2+} was visible blue, in contrast with the following brown NH_4^+ band. The three packed columns were repeatedly used in a merry-go-round way. After that the Cu^{2+} adsorbed 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 temperatures of the columns were kept constant at 288 ± 0.2, 333 ± 0.2, and 353 ± 0.2K, by circulating the thermostat water through the water jackets surrounding the columns. The apparatus used for the separation of copper isotopes is similar to that used for Eu isotope separation by ethylenediaminetetraaceticacid (EDTA) (13). The experimental conditions are summarized in Table 1.

Analysis

The concentration of Cu in each fraction of the effluents was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES) system, Model SPS 1500VR, Seiko Instruments Inc., Chiba, Japan, at a 381.967 nm wavelength after 1000 times dilution of the samples. The ^{63}Cu/^{65}Cu isotopic ratios of copper were determined by using a MAT 261 mass spectrometer, Varian MAT GmbH Bremen, Germany 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. The samples had to be pretreated before being analyzed by the mass spectrometer. A portion of each sample fraction was burned by a burner in order to remove the organic compounds. The burned samples were treated by concentrated HNO_3 and heated to dryness on a hot plate. On the basis of these conditions, each prepared copper sample was diluted with 0.5 *M* HNO_3 then, a drop of the copper solution [20 μg $Cu(NO_3)_2$] sample was placed on the surface of a vaporizing filament and dried

Table 1. Experimental Conditions

	Temperature		
	288K	333K	353K
Resin	Strongly acidic cation exchange resin (TITECH-3, 37–88 μm)		
Column size	0.8 cm I.D. and 100 cm length		
Feed solution	0.5 *M* $CuSO_4$ + 0.7 *M* H_2SO_4		
Eluent	0.06 *M* ammonium malate (D,L) at pH = 5.5 adjusted by NH_4OH		
Band length (cm)	40	44	52
Migration length (cm)	592	592	1474
Flow rate (cm^3/min)	0.32	0.31	0.30
Band velocity (cm/min)	0.067	0.068	0.071

by heating with an electric current of about 1–2 A for 1 min. Later on, the sample filament unit was inserted into the ion source of the mass spectrometer and the vacuum system was started. When the pressure was reduced to $\sim 2 \times 10^{-8}$ the ionization current was slowly increased by 0.2 A every 3 min in a stepwise manner. Cu ion beam appeared when the ionization filament current reached ~1.7 A. No electric current was applied to the vaporization filament. After setting the magnetic field, the ^{63}Cu and ^{65}Cu mass peaks were repeatedly recorded by a Faraday cup collector. 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.

RESULTS AND DISCUSSION

Chromatographic Processes

The chemical exchange reactions involved in the present system first take place at the interface between NH_4^+ and Cu^{2+} adsorbed bands. When $(NH_4)_2$ malate reached the front boundary of the Cu^{2+} adsorbed band, the malate species is transferred to Cu^{2+} because of the large stability constant of the Cu–ligand complex formation compared to that of ammonium ion, Eq.(2). During the moving down of the Cu–ligand complex species through the Cu^{2+} adsorbed band in the column, the isotopic exchange reaction takes place between Cu^{2+} ions in the resin phase and Cu–ligand complex species in the solution phase, Eq. (3). After that the Cu–ligand complex reaches the H^+ ion band, where the ligand is transferred to H^+ ions, and the Cu^{2+} ions are adsorbed in the resin phase, Eq. (4). By this way, the two ends of the band are recycled. This gives a chance for higher enrichment at the two ends of the band, which is the major advantage of using band displacement chromatography over other chromatographic processes like breakthrough and reverse breakthrough chromatography. The use of band displacement chromatography is highly recommended in isotope separation due to the small separation coefficient values usually encountered in these separation processes. Besides, in this mode, we can calculate the values of the separation coefficients two times, from each boundary's isotopic analysis data. This will give us a chance to recheck the calculated values by taking the average of the two values of each isotope pair. The relating chemical reactions could be expressed, in the simplest form, as

$$(NH_4)_2\text{–}L + \underline{Cu}^{2+} \rightarrow 2\underline{NH_4^+} + Cu\text{–}L \qquad (2)$$

$$^{65}\underline{Cu}^{2+} + {}^{63}Cu\text{–}L \leftrightarrow {}^{63}\underline{Cu}^{2+} + {}^{65}Cu\text{–}L \qquad (3)$$

$$Cu\text{–}L + \underline{2H}^{+} \rightarrow \underline{Cu}^{2+} + L\text{–}2H \qquad (4)$$

where the underlines represent the species in the resin phase and L represents the ligand. Due to the fact that the isotope effects of copper are small, long distance migration is necessary to measure the isotope separation coefficient. The chromatogram of Cu in the LXS after long migration, the pH, and the isotope abundance ratio observed in the displacement band are shown in Figs. 1–3. The dotted lines show the isotopic abundance ratio in the feed solution. It can be seen that the heavier isotope ^{65}Cu is enriched into the front part, or preferentially fractionated in the complex form in the solution phase. This tendency is the same as that observed in the chromatographic isotope separation of calcium (7,8), magnesium (9), strontium (10), gadolinium (25), europium (13), and copper (16). Since the heavier isotope is enriched in the complex species, the observed isotopic enrichment tendency accords with the theoretically expected direction of the isotopic effects in chemical exchange based on the molecular vibration theory.

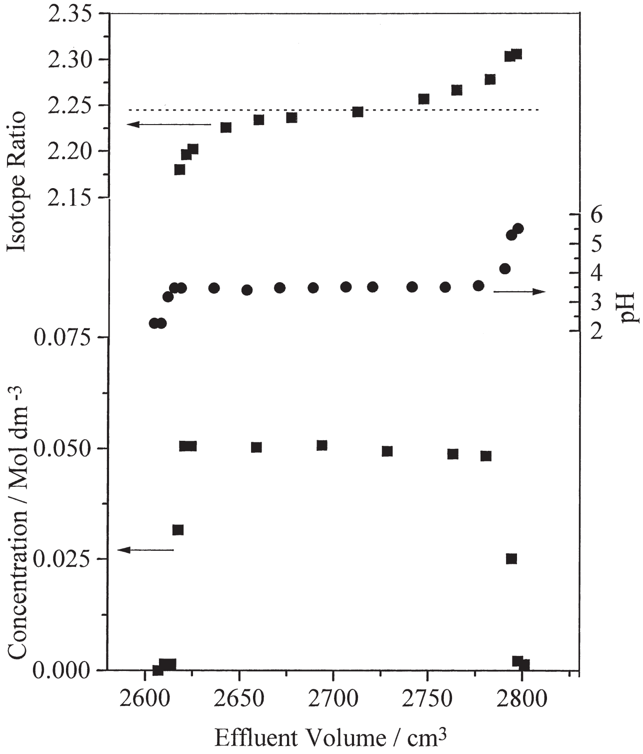

Figure 1. Chromatogram, pH, and the isotopic distribution in the Cu band displaced at 288K.

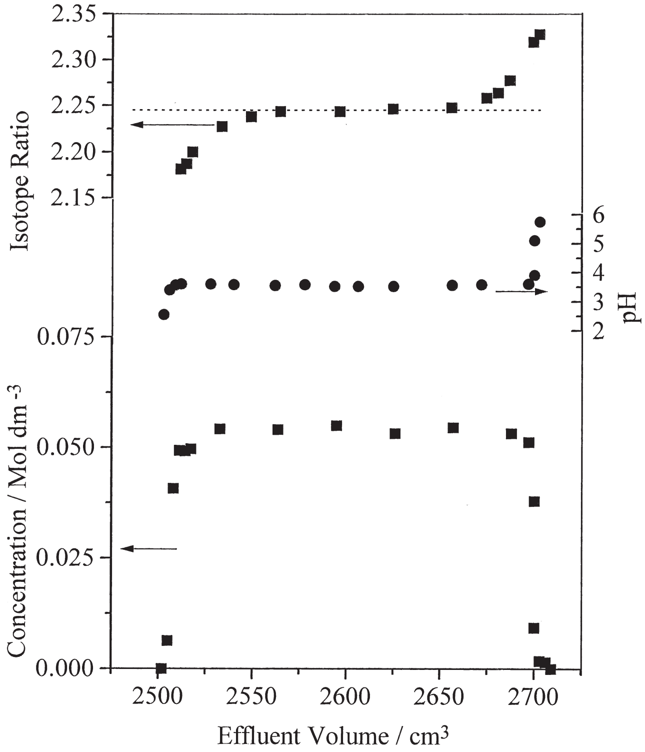

Figure 2. Chromatogram, pH, and the isotopic distribution in the Cu band displaced at 333K.

The concentration of Cu in the plateau region of the chromatogram, 0.055–0.058 mol, is not exactly equal to the concentration of the ammonium malate in the eluent feed, 0.06 mol, which suggests that the ligand/copper ratio is less than 1. The excess ligand is assumed to be coordinating with H^+ ions initially sorbed mixing with Cu band (25). This is supported by the low pH value of the plateau region of the chromatograms as shown in Figs. 1–3. In fact, the chemistry of the system may be much more complicated than that represented by Eqs. (2)–(4). The exact complex structure and the different possibilities of Cu and/or H_2O hydrolysis are out of the scope of the present work.

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

$$S = ([^{63}\underline{\mathrm{Cu}}]/[^{65}\underline{\mathrm{Cu}}])/([^{63}\mathrm{Cu}]/[^{65}\mathrm{Cu}]) \tag{5}$$

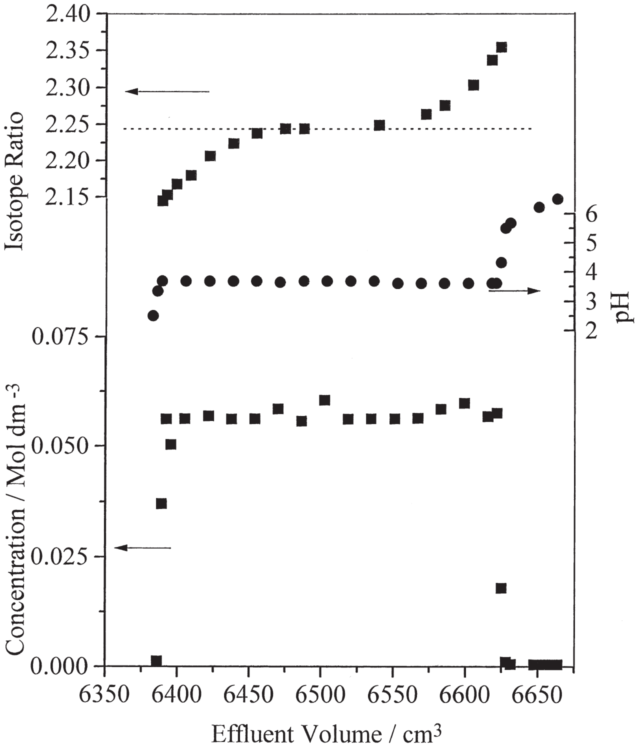

Figure 3. Chromatogram, pH, and the isotopic distribution in the Cu band displaced at 353K.

where the underlines indicate the resin phase. The separation coefficient, ε, values calculated directly from the experimentally observed isotopic enrichment curves at the front boundaries and the rear boundaries of the chromatograms gave high error values due to the error in the isotope ratio values measured by the mass spectrometer. In fact, the isotopic analysis of Cu is much more difficult and higher errors were encountered compared to many other elements like U and Eu. To reduce the error values, the isotope ratios of the front boundaries and the rear boundaries of the chromatograms were first fitted to the equation:

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

where k is the slope coefficient (27). This fitting gave straight lines. An example of that fitting is shown in Fig. 4 for the run carried out at 333K. Some irregular points were removed, and then the straight-line equations were used to estimate the isotope ratio values. The estimated values of the isotope ratios were used to

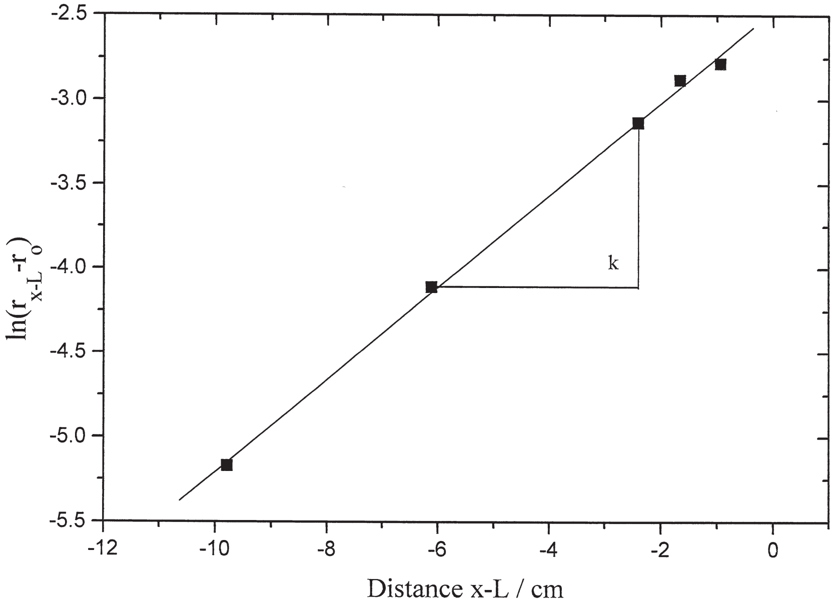

Figure 4. The relation between the isotope enrichment degree $\ln(r_{x-L} - r_o)$ and the distance from the band end $(x - L)$ for the ion exchange chromatogram carried out at 333K.

calculate the separation coefficients as previously reported (6,16,26).

$$\varepsilon = \sum q_i |R_i - R_o| / QR_o(1 - R_o) \quad q_i = C_i V_i \tag{7}$$

where q_i, R_i, C_i, V_i are the amount of copper, the isotopic fraction of ^{63}Cu, the concentration of the copper, and the effective volume of the sample fraction i, respectively. R_o denotes the isotopic fraction of the original feed and Q is the total ion exchange capacity of the resin for copper under the experimental conditions. The summation is taken over all the fractions for the front boundary part enriched in ^{63}Cu, ε_f, and for the rear boundary part depleted of ^{63}Cu, ε_r, which in turn was used to calculate the average values and the errors of the separation coefficient values shown in Table 2.

Apparently, the values of ε decrease with the increase in the temperature, which is the usual pattern of the heavy elements chemical isotope effects based on the quantum effects of the molecular vibrations. The same trend of the temperature effect was observed in the study of the lithium (17), rubidium (18), Cu(I)–Cu(II) (19), boron (20), U(IV)–U(VI) (28), uranium(IV)–malate, citrate, and lactate systems (21).

Table 2. The Separation Coefficient and the Height Equivalent to a Theoretical Plate (HETP) at Different Temperatures

Temperature (K)	Separation Coefficient ($\varepsilon \times 10^{4}$)	Height Equivalent to a Theoretical Plate (cm)
288	2.87 ± 0.28	0.041
313[a]	2.8 ± 0.20	Not available
333	2.39 ± 0.27	0.033
353	2.13 ± 0.26	0.030

[a] Reference (16).

The calculated values of the separation coefficients were fitted against $1/T^2$, according to the molecular vibrations theory, as shown in Fig. 5. This supports the previously mentioned result that the isotope effects of Cu, in this system, are in fact due to the quantum effects of the molecular vibrations. As can be seen from Fig. 5, the separation coefficients of the present system agree with data previously reported at 313K (16), within the experimental error.

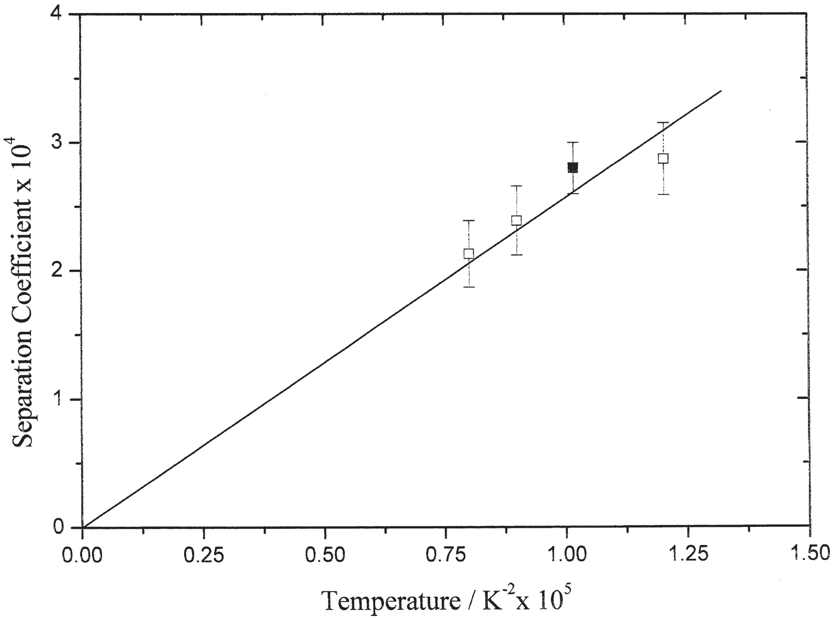

Figure 5. Effect of temperature on the separation coefficient of copper isotopes, ■ Ref. (16).

The height equivalent to a theoretical plate is considered as one of the parameters used to determine the performance of any chromatographic separation system. The smaller the value of HETP, the shorter the migration length needed for a specific separation task i.e., the higher the efficiency of the system. The value of HETP can be calculated from Eq. (8) (27):

$$\mathrm{HETP} = (\varepsilon/k) + (1/k^2 L) \tag{8}$$

where L is the total migration length and k is the slope coefficient, the slope of the $\ln(r - ro)$ vs. $x - L$ plot (27). Figure 4 shows a typical example of such a fitting in the case of the run carried out at 353K. The values of HETP, at different operating temperatures, have been calculated using Eq. (8) for both the front and rear boundaries. The average values were calculated and are given in Table 2. The values of the HETP reported in this work are almost equal to the values of the HETP reported for the Cu(I)–Cu(II) system and both are very small compared to the case of boron isotope separation by anion exchange resin; HETP = 0.18 cm (28). The results show that HETP decreased from 0.041 to 0.03 cm with the increase in temperature from 288 to 353K. This could be due to the fact that the increase in the temperature increases the energy and the mobility of different ions, which in turn, increases the rate of reaction and reduces the HETP.

CONCLUSIONS

The ideal displacement chromatogram in the copper LXS was obtained using ammonium malate as a ligand for a relatively long migration. The heavier isotope ^{65}Cu was clearly found to be enriched at the front boundary and the lighter isotope ^{63}Cu was enriched at the rear boundary of the Cu adsorbed band at all temperatures. The value of the separation coefficient was found to decrease with the increase in the temperature, which agrees with the molecular vibration theory.

The HETP, was calculated and found to decrease from a value of 0.041 cm at 288K to a value of 0.03 cm at 353K.

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