The Effect of Temperature on Uranium Isotope Effects Studied by Cation Exchange Displacement Chromatography

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The uranium isotope effect in the exchange system uranyl(VI)-malate ligand at 288–343 K has been studied by ion exchange displacement chromatography. At all temperatures ^{235}U is enriched at the front of the uranium band. The single stage separation coefficient, ($\varepsilon = \alpha - 1$), increased from $(0.9 \pm 0.1) \times 10^{-4}$ at 288 K to $(2.9 \pm 0.3) \times 10^{-4}$ at 343 K. The equilibrium constant of the isotope exchange reaction equaled the separation factor at the current experimental conditions. The increase of the separation coefficient with temperature, which is in contrast to the uranium(IV)-ligand exchange systems, can be explained by the introduction of the field shift effect.

Key words: Isotope Effects; Chromatography; Separation.

Introduction

After the lithium isotope separation by ion exchange chromatography by Taylor and Urey [1], different systems, such as solvent extraction [2], amalgam/aqueous solution and amalgam/organic solution [3, 4], ion exchange electromigration and ion exchange displacement chromatography [5–7], were applied to study the isotope effects by chemical exchange reactions. Regardless the chemical exchange system used, the molecular vibrations were believed to be the main, factor that affect the isotope exchange reactions of heavy elements. This belief was based on the relationship between the equilibrium constant of the isotopic exchange reactions and the reduced partition function ratios, RPFR, shown by Waldmann and by Bigeleisen and Mayer [8] in 1943 and in 1947, respectively. But during the systematic experimental and theoretical investigations on the isotope effects in chemical exchange systems carried out through the last two decades this belief became doubtful. The anomalous ^{235}U–^{238}U isotope effect in U(IV)–U(VI) chemical exchange shown by the present authors (M. N. and Y. F.) could not be explained by the molecular vibration theory [9]. Later on, the same trend was found in the case of ^{233}U isotope effects [10]. It was suggested that the isotope effects in the U(IV)–U(VI) exchange system arise mainly from the interaction between the nuclei and the electrons in the isotopes. Nishizawa has suggested anomalous mass effects in lighter elements such as Zn [11]. This was attributed to the isotope shift in the orbital energy. Bigeleisen has shown that the field shift becomes the major effect in the isotopic chemical exchange systems of uranium [12]. Recently, the anomaly of ^{155}Gd–^{157}Gd isotope effects in ligand exchange reactions observed by ion exchange chromatography were studied and found to be due to the shape and size of the nucleus [13].

Studying the temperature effect on the equilibrium constant of isotopic chemical exchange reactions is a powerful tool for analyzing the isotope effects. It can help in determining which is the major factor that affects the isotope effects, molecular vibrations or the field shift. If the equilibrium constant was found to be inversely proportional to the square of temperature, the molecular vibration is considered as the main factor. On the other hand, the field shift would be considered as one of the main factors if the equilibrium constant was found to increase with the temperature. This trend was observed in the case of europium [7] and barium [3].

By studying the temperature effect, a better understanding of the origin of the isotope effects would be achieved. So, this work was carried out to study the effect of temperature on the separation of uranium isotopes by using ion exchange chromatography based on a uranium-ligand exchange system.

Experimental

Ion Exchange Resin and Reagents

The ion exchange resin was a macroporous strongly acidic cation exchange resin, (Bio-Rad AG-MP 50, 100–200 mesh size). All other reagents were of analytical grade and were used without further purification.

Preparation of Uranium(VI)-Malate Feed Solution

Uranium(VI)-malate feed solution was prepared by feeding UO_2 $(NO_3)_2$ to a small column packed with the resin until the uranium band reached a suitable length. The band was eluted by feeding a 0.2 M ammonium malate solution at pH 7.6. The band length usually changes during the formation of uranium(VI) malate complex, and this is the reason why the complex was prepared in a separate column. When the band was eluted from the column, the outermost ends of the band were cut and removed to assure that no isotopic effect was present in the feed solution. The bulk of the band was collected and used as a feed solution to the main column.

The Chromatographic Process

Two glass columns, 210 cm in length and 1 cm in diameter, were connected in series with a teflon tube, 1 mm in diameter, and were packed with the cation exchange resin, Bio-Rad AG-MP 50. When the total migration length needed was 2 meters only, one column was used. A 2 M HCl solution was fed to the column to remove any impurities and to convert the resin into the H^+ form. Uranium(VI) malate solution was fed to the column until a suitable length of the uranium(VI) malate band was reached. Then the ammonium malate solution at pH 7.6 was fed to the column to elute the band in the band displacement manner. The temperature of the columns was kept constant by circulating thermostated water through the water jackets surrounding the columns. The operational temperatures were (288 ± 0.2), (313 ± 0.2), (323 ± 0.2), and (343 ± 0.2) K. When the band started to elute from the column, the effluent was collected in small fractions and subjected to concentration and isotope analysis. The experimental conditions are summarized in Table 1.

Analysis

The uranium concentration was determined by photospectrometry and the isotope ratio by using a mass spectrometer MAT 261 equipped with a thermal ionization ion source. The UV-Visible spectra of uranyl malate were scanned from 190 to 1100 nm by means of a HEWLETT PACKARD HP 8453 UV-Visible spectrophotometer using a thermally controlled cell.

Results and Discussion

Chromatographic Process

The chromatography of the uranyl-malate complex formation system was carried out in the temperature range 288–343 K using the band displacement technique. The chromatography apparatus used is similar to that used for the study of gadolinium [13] and copper isotope effects [14]. When the ammonium malate solution fed to the column as eluent reached the rear boun-

Table 1. Experimental conditions of uranyl-malate system.

Temperature	288 K	313 K	323 K	343 K
Resin		Bio Rad AG-MP 50, 100–200 Mesh Size		
Pretreatment		2 M HCl followed by distilled water to convert the resin into H^+ form		
Eluent		0.2 M ammonium malate at pH = 7.6		
Feed solution		0.2 M U(VI)-malate		
Column size		1.0 cm I.D. and 200 cm length		
Band height	25.5	23.5	21	21.5
Migration length	2 m	4 m	2 m	2 m
Flow rate	0.89 cm^3/min.	0.90 cm^3/min.	0.64 cm^3/min.	0.84 cm^3/min.
Band velocity	0.30 cm/min.	0.28 cm/min.	0.18 cm/min.	0.29 cm/min.
M	2.03	1.95	1.9	2.08

Where *M* is the average number of the ionic charge of the uranyl species in the resin phase.

dary of the U(VI) sorbed band, the complex was transferred into the uranium complex due to the larger stability constant of the U(VI)-malate complex species compared to the resin-found species according to

$$(NH_4)_2 \cdot L + (\underline{UO_2})^{2+} \rightarrow UO_2 \cdot L + 2\,\underline{NH_4^+}, \quad (1)$$

where L is the malate group and underlining represents the resin phase. The uranyl malate complex passed down through the $(UO_2)^{2+}$ sorbed band giving the chance for an isotopic exchange reaction

$$^{238}UO_2 \cdot L + {}^{235}(\underline{UO_2})^{2+} \rightarrow {}^{235}UO_2 \cdot L + {}^{238}(\underline{UO_2})^{2+}. \quad (2)$$

At the front boundary, the U(VI) malate complex in the solution was in contact with the resin in the H^+ form, giving a chance for the reaction

$$\underline{2\,H^+} + UQ_2 \cdot L \rightarrow L \cdot H_2 + (\underline{UO_2})^{2+} \quad (3)$$

to take place.

The chromatograms of uranium, the pH of the band and the isotopic abundance ratios observed at the front boundaries of the displacement bands at 288, 313, 323, and 243 K are shown in Figs. 1–4. The concentration analysis of the uranyl band shows that the U concentration in the band was 0.2 M, which is the same concentration as that of the ammonium malate solution used as eluent at all temperatures. Potentiometric studies of uranyl malate aqueous solutions have indicated that, in the pH range 2–4, the present species are predominantly 2:2 binuclear chelates [15]. As the pH of the uranyl malate band was within that range almost constant at of (2.05 ± 0.05), as shown in Figs. 1–4, a ratio of 2:2 is assumed for the uranyl malate complex, and the existence of other complexes is not expected. An ideal sharp boundary was not achieved in the rear parts of the chromatograms, as can be seen from these chromatograms. Only the front boundary was sharp enough at all temperatures and became sharper as the temperature increased. This could be attributed to the fact that the difference between the stability constants of ammonium malate and uranyl malate is not as large as the difference between the stability constants of uranyl malate and malic acid. In general, the larger the difference between the stability constants of the complex species in two successive bands, the sharper the boundary between these two bands. According to the theory of isotope distribution between two phases developed by Kakihana [16], a sharp boundary is an essential condition for calculating the separation coefficients. Therefore the separation coefficient can be calculated only from the data of the front boundary. This is the reason why the isotope ratios were measured only for the front boundaries. The dashed lines in Figs. 1–4 show the isotopic abundance ratio in the feed solution.

As can be seen from Figs. 1–4, ^{235}U is enriched in the front part, or preferentially fractionated into the complex form in the solution phase at all temperatures. This tendency agrees with the pervious findings for the U(VI) malate system reported by Kim et al. [17], while it is opposite to the tendency observed for the isotope effects of U(IV) malate, U(IV) lactate and U(IV) citrate systems [18].

Separation Factor

The single stage separation factor, $S = (1 + \varepsilon)$ for the $^{235}UO_2/^{238}UO_2$ isotopic pair is defined here as

$$S = ([^{238}\underline{UO_2}]/[^{235}\underline{UO_2}])/([^{238}UO_2]/[^{235}UO_2]), \quad (4)$$

where the species in the resin phase are underlined. As we did not measure the isotopic ratios of the rear boundaries, there will be some suspicious that remixing between the enriched part and the depleted part may have taken place in the middle part of the uranium band. To explore this possibility, $Ln\,(r - r_0)$ vs. $x - L$ was plotted for the four runs [19]. As can be seen in Fig. 5, straight lines were obtained in the four cases, assuring that there is no remixing in the four runs. Therefore the separation coefficients, ε's, were calculated using the isotopic enrichment curves of the front boundaries according to the equation developed by Spedding [20], and Kakihana [21].

The isotope-separation coefficients, ε, at different temperatures are shown in Table 2. These values agree, within the experimental error, with the previously reported value at 298 K [17].

Apparently ε increases with increasing temperature. This trend is opposite to the trend observed for isotope

Table 2. Separation coefficients due to field shift and molecular vibrations effects of the U(VI)-malate system.

Temperature/K	FS/10^4	MW/10^4	$\varepsilon(\ln K)/10^4$	
			Calculated	Experimental
288	15.5	–14.5	1.2 ± 0.2	0.9 ± 0.1
298	14.9	13.3	1.7 ± 0.2	2.2 ± 0.2*
313	14.2	–12.0	2.2 ± 0.3	1.4 ± 0.4
323	13.8	–11.3	2.5 ± 0.3	2.3 ± 0.5
343	13.0	–10.0	3.0 ± 0.3	2.9 ± 0.3

* Reference [17].

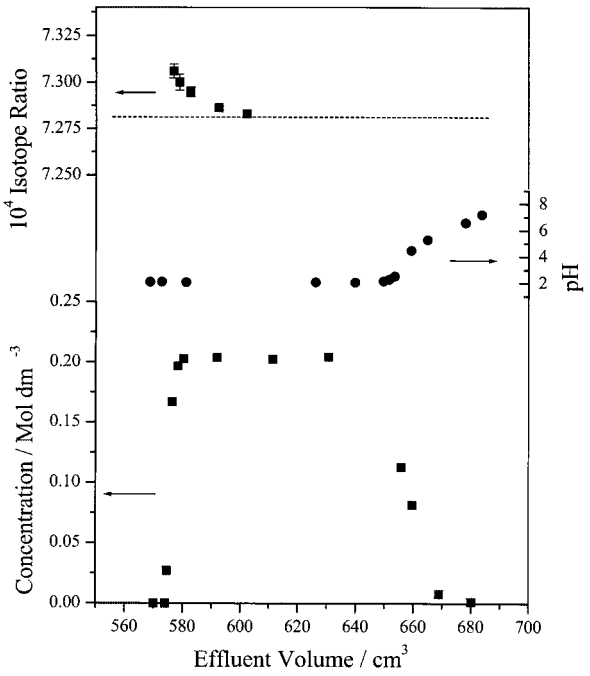

Fig. 1. Concentration profile, pH and isotopic abundance ratio of the uranium ion exchange chromatography at 288 K.

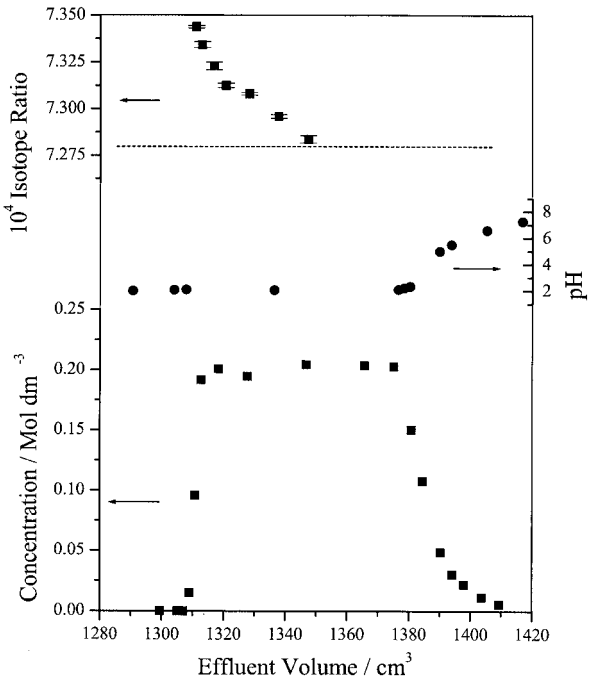

Fig. 2. Concentration profile, pH and isotopic abundance ratio of the uranium ion exchange chromatography at 313 K.

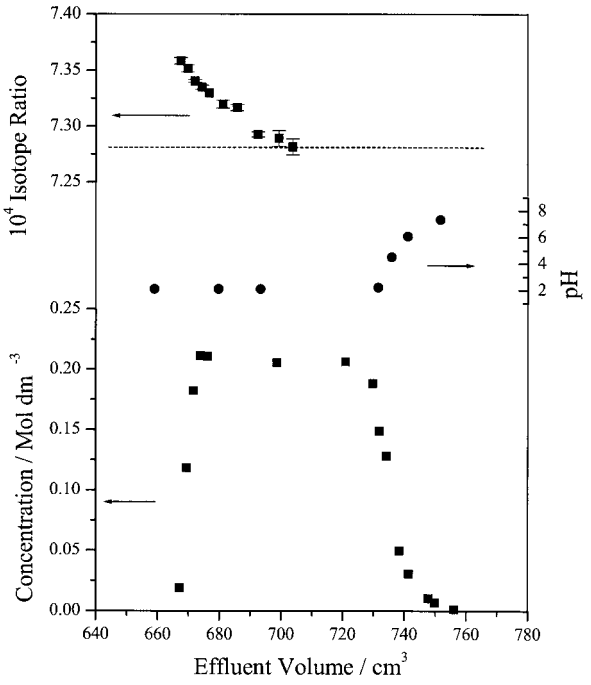

Fig. 3. Concentration profile, pH and isotopic abundance ratio of the uranium ion exchange chromatography at 323 K.

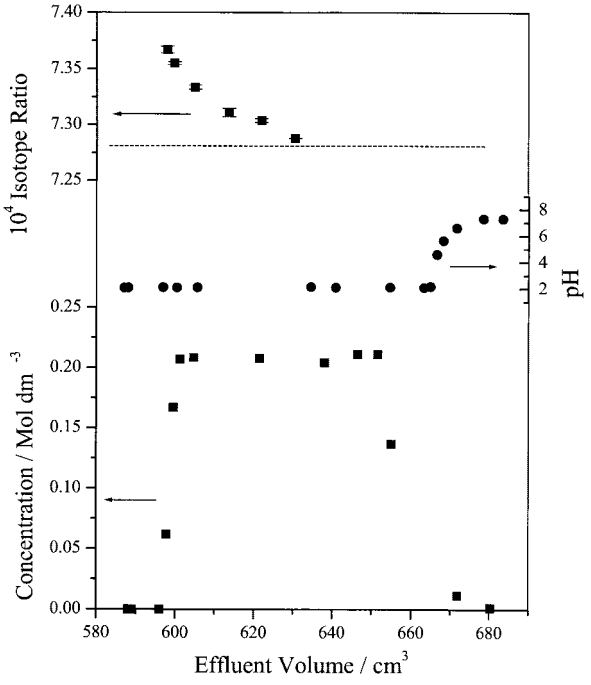

Fig. 4. Concentration profile, pH and isotopic abundance ratio of the uranium ion exchange chromatography at 343 K.

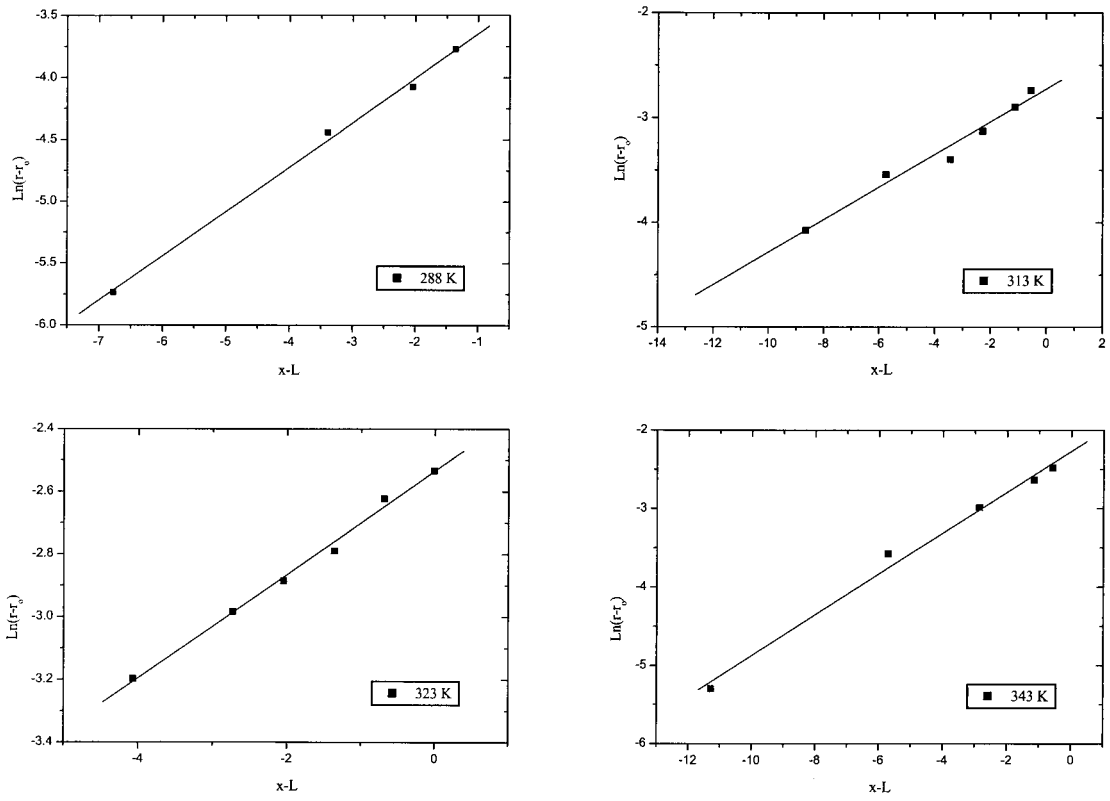

Fig. 5. Plot of $Ln\,(r-r_0)$ vs. $x-L$.

effects of uranium in U(VI)/U(IV), U(IV)/malate, U(IV)/lactate, U(IV)/citrate systems. Such an inverse temperature effect is different from the usual pattern of heavy-element chemical isotope effects based on the quantum effects in molecular vibration. However, a similar trend of the temperature effect was observed for the europium isotope effects in Eu(II)/Eu(III) exchange chromatography [7] and for the barium isotope effects in the amalgam/aqueous hydroxide solution system carried out by Chang [3]. This was also the case for the U(VI) citrate system, where the separation factor increased from 1.6×10^{-4} to 1.8×10^{-4} as the temperature increased from 298 to 333 K [22].

Isotopic Equilibrium Constant

Based on the above results, the discussion can be extended to the isotopic equilibrium constant *K*. To assure that the two species do not coexist in one phase, both phases have to be analyzed. In the solution phase, as mentioned above, based on the concentration analysis and potentiometric studies previously reported [15, 23] the only uranyl species is the 2:2 binuclear uranyl malate complex. It is expected that the stability constants of most of the complex species change with temperature. So, to assure the coordination form of the uranyl malate complex, the UV-Visible spectrum of uranyl malate was studied in the temperature range 298–323 K. Figure 6 shows that the spectra obtained at all temperatures are almost equal. This means that the uranium complexes in the solution phase are almost the same in all chromatographic runs. In the resin phase, the average ionic charge of the uranyl species, *M*, has to be calculated. This was carried out according to the method developed by Okamoto et al. [24]. The resultant values of *M* at different temperatures were found to be 2 ± 0.1, as shown in Table 1. Therefore it is possible to assume that only hydrated uranyl species exist in the resin phase, and only uranyl malate complex species exist in the solution phase, and the values of the isotopic equilibrium con-

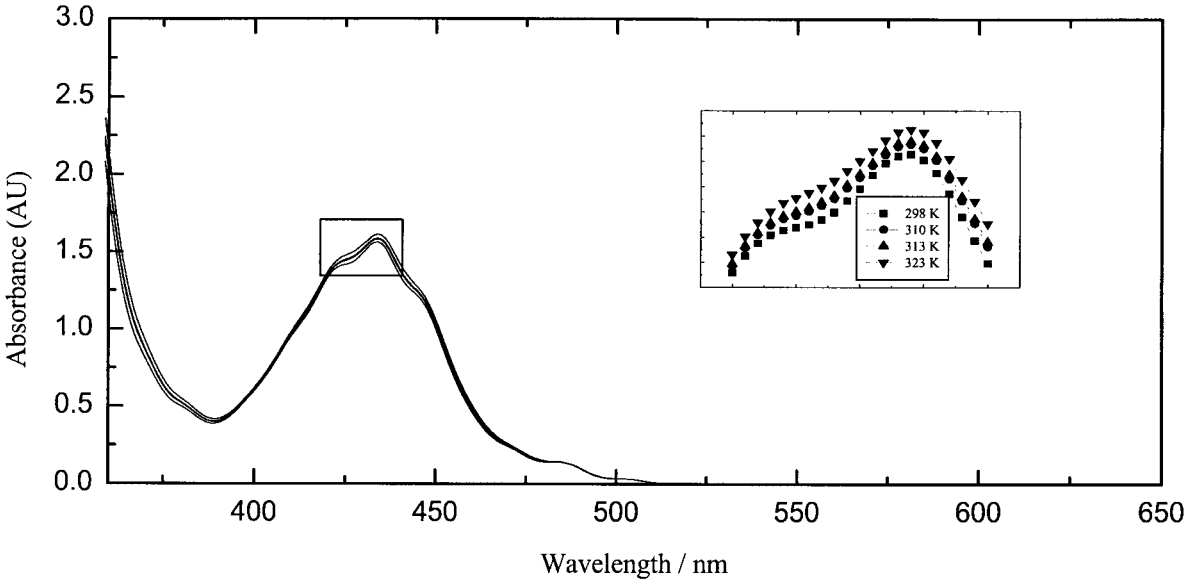

Fig. 6. Effect of temperature on the uranyl malate spectra.

stant K is equal to the value of the separation factor, $\alpha = 1 + \varepsilon$, at the different temperatures. Moreover, due to the fact that the separation coefficient of heavy isotopes is small, the separation coefficient, ε, will be equal to $\ln K$.

According to the study of the lithium isotope effects [25], magnesium and barium [3] isotope effects in amalgam systems, and europium [7] isotope effects in ion exchange displacement chromatography systems, the dependence of $\ln K$ or ε on temperature can be given by

$$\varepsilon = \ln K = A/T^2 + B/T,$$

where A, B are constant with opposite signs. In the case of the U(IV)–U(VI) exchange reaction it was proved that the first term in (5) represents the molecular vibrations effect, and the second one represents the field shift effect [12]. The calculated values of the separation coefficients of the U(VI) malate system are plotted versus $1/T$ according to (5) over a wide temperature range in Figure 7. The constants A and B of (5) are calculated for the U(VI) malate system as –118 and 0.45, respectively. Table 2 shows the contribution of the molecular vibrations, MV, and field shift effect, FS, to $\ln K$ of the U(VI) malate system at different temperatures. The results of the temperature dependence of $\ln K$ show that the major isotope effect comes from the field shift effect.

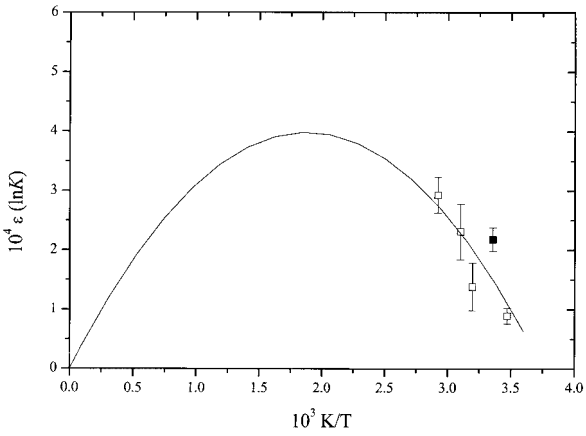

Fig. 7. The separation coefficient, $\varepsilon(\ln K)$, as a function of temperature over a wide temperature range. □, this work; ■, reference [17].

Molecular Vibrations

The molecular vibrations effect can be expressed by the Bigeleisen-Mayer equation as

$$\ln K = \ln f\left(\frac{238}{235}\right)_{\text{resin}} - \ln f\left(\frac{238}{235}\right)_{\text{complex}},$$

where f is the reduced partitioning factor ratio, RPFR, while 238 and 235 represent ^{238}U and ^{235}U, respective-

ly. The negative sign of the molecular vibrations effect term in the case of the U(VI) malate system, shown in Table 2, indicates that the RPFR of the U(VI) malate species, in solution phase, is greater than that of the uranyl hydrated species in the resin phase. Accordingly, ^{238}U is enriched in the complex form. The molecular vibration effects have an opposite direction of enrichment to the actual one.

It is believed that the uranyl ions exist in the resin phase as aqua-ions with a most probable hydration number of 5 [26]. The five oxygen atoms of hydration water molecules are symmetrically coordinating to the U atom in a plane perpendicular to the O = U = O axis. Oi and Kakihana [26, 27] thoroughly studied this ion by means of internal coordination analysis. They found that this ion has 18 normal modes of vibrations, 7 are degenerated and 4 non-degenerated. Among the resultant 11 vibrational frequencies only 5 can give isotope shifts, U = O asymmetric stretching, O = U – L bending, U – L asymmetric stretching, O = U = O bending, and L – U – L bending. The RPFR, calculated by this analysis, was found to be 0.0002. The contribution of ν_3, U = O asymmetric stretching, to the total RPFR was found to be 52.5%. Although a similar precise normal coordinate analysis of the uranyl malate complex has not been done, yet, due to the lack of spectroscopic data, a rough one can be presented. The structure of the 2:2 uranyl malate complex, which has been reported by Rajan and Martell [15], is very complicated for molecular vibrational analysis. According to this structure, the U atom is coordinating with several oxygen atoms, 2 hydroxyl, 2 carboxylic and *x*, most probably $x = 1$, water of hydration. Thus, a similar coordination analysis to that of the uranyl aqua-ion is obtained with the only exception that the five oxygen atoms are not symmetrically coordinating to the U atom. By analogy to the uranly-aqua ion, it is expect to have 5 similar vibrational frequencies that can give isotope shifts like those of the uranyl-aqua ion, but with different values. Besides, several numbers of vibrational frequencies that can give isotope shifts are expected due to the unsymmetrical coordination. Unfortunately only ν_3, the U = O asymmetric stretching, has been measured. It was found to be 962.4 cm^{-1} in the case of the uranyl-aqua ion [23] and to decrease to 916.2 cm^{-1} in the case of U(VI) malate [17, 23]. This reduction in the energy of ν_3, which is accompanied by bond elongation in case of the U(VI) malate species, is believed to be due to the stronger coordination of the U atom by the oxygen atoms of the malate ligand. It can be assumed that the contributions of the other 4 vibration bands also increase. If we further take into consideration the contribution of the unmeasured vibrational frequencies that can give isotope shifts, it is possible to assume that the RPFR of U(VI) malate species is greater than that of the uranyl-aqua ions in the resin phase. A further experimental study of the vibration frequencies is needed to assure that assumption.

Field Shift

The field shift usually leads to an enrichment of the heavy isotope in the species in which the electron density at the nucleus is minimum [12]. If the U atom is more strongly coordinated to the oxygen atoms of the malate ligand than to the water molecules, the oxygen atoms of the former case are closer to the U atom and donating more electron density, which leads to an enrichment of the heavier isotope ^{238}U on the aqua ion side, as was shown experimentally.

Conclusions

The ion exchange chromatography of the U(VI) malate exchange system was studied in the temperature range 288–343 K. The lighter isotope ^{235}U was clearly found to be enriched in the uranyl malate species in the solution phase at all temperatures, and the isotope separation coefficients, ε, increases with the temperature. The relation between logarithm of the equilibrium constant, $\ln K$, and temperature accords well with the theory developed for the field shift isotope effect proposed by Bigeleisen. The contribution of the field shift effect and the molecular vibrations effect to $\ln K$ was calculated for all pertinent temperatures. The major factor that affects the isotope effects in the uranyl malate exchange system is suggested to be the field shift effect. The molecular vibrations effect alone would enrich the heavier isotope ^{238}U in the uranyl malate species.

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