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Separation of vanadium isotopes by ion-exchange chromatography

Yong-Hong Zhang, Masao Nomura, Masao Aida, Yasuhiko Fujii*
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

Abstract

Cation-exchange displacement chromatography of VO^{2+} was carried out for studying vanadium isotope effects in carboxylate ligand-exchange systems. The heavier isotope ^{51}V was enriched in the carboxylate complex solution. The isotope separation coefficients $\epsilon(=\alpha-1)$ for $^{50}V/^{51}V$ were $2.2\cdot10^{-4}$ and $2.4\cdot10^{-4}$ for citrate and lactate systems at 298 K, respectively. These values are much larger than those obtained in a previous study on the malate system. The existence of binuclear complexes of VO^{2+} may create the conditions for larger isotope fractionation. From the viewpoint of the process development of isotope separation, the heights equivalent to a theoretical plate of these processes were analyzed and found to be very small in each system due to the homogeneous, small and highly porous resin used. Citrate may be better than the other tested systems for the vanadium isotope separation.

Keywords: Isotope ratio; Height equivalent to a theoretical plate; Vanadyl carboxylate; Metals

1. Introduction

Vanadium is a ubiquitous element dispersed throughout the earth's crust, rivers, lakes, and oceans, and consists of a mixture of only two naturally occurring isotopes with mass numbers 50 and 51. The geochemical and biological behaviors of vanadium have recently received considerable attention, because this element is classified as a trace bio-element [1,2]. It has long been known that vanadium is highly accumulated in some petroleum in the form of vanadyl-porphyrins and in the blood of certain invertebrates. Furthermore, significant fractionations in the $^{50}V/^{51}V$ isotopic ratio were observed in these organic materials [3,4]. So far there has been little work on the related physicochemical study of vanadium isotope effect.

Since Taylor and Urey first applied the chromatographic adsorption method to the separation of lithium isotopes in 1938 [5], there have been many investigations and studies on isotope effects and separations by chemical-exchange processes [6] ranging from hydrogen to uranium. In our laboratory, starting from U [7,8], the experimental work was extended to the transition metal elements Zn [9] and Cu [10], and lanthanoid Eu [11] and Gd [12] in ligand-exchange reaction by ion-exchange chromatography for the study of the isotope effect and separation. Recently, our attention has turned to another highlighted transition metal element—vanadium, due to its considerable geological and biological significance.

In the previous experimental work on uranium isotope effects in uranyl complex-formation systems using ion-exchange displacement chromatography, the results showed that the lighter isotope ^{235}U is

*Corresponding author. Tel.: +81-3-5734-2378; fax: +81-3-5734-2958.
E-mail address: yfujii@nr.titech.ac.jp (Y. Fujii).

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enriched in the uranyl carboxylate complexes, and among some selected uranyl carboxylate complexes, the malate ligand system showed the largest separation coefficient [8]. In addition, copper isotope separation was carried out in malate ligand-exchange chromatography and a large separation coefficient was also obtained [10]. Accordingly, in previous work, we also selected malate as a ligand and applied it to a study of vanadium isotope effects in vanadium complex formation [13]. However, the result was against expectation, i.e., the separation coefficient observed in the vanadium isotope separation process by the same method is much smaller than that obtained in uranium and copper isotope enrichment in the malate complex system. The result from vanadium experimental work in the malate system also demonstrated that the heavier isotope is enriched at the front boundary of the VO^{2+} band, which follows the general rule based on the quantum molecule vibration energy that the heavier isotope preferentially fractionates into a strongly-bound complex in aqueous solution phase. In the above-mentioned uranium experiment, besides the malate system, the separation coefficients in citrate and lactate systems were also obtained. In light of these observations it is interesting to consider applying citrate and lactate as ligands to vanadium isotope separation study to see what results would come about in these two systems.

Malic, citric and lactic acids are important components of biological systems and are commonly found in plants and animals and are directly related to glucose metabolism [14]. They form a wide variety of complex species with metal ions and usually act as a bidentate or tridentate ligands through the hydroxyl and the carboxyl oxygen atoms [15]. The knowledge of complex equilibria involving VO^{2+} in the presence of likely biological ligands is relevant for the understanding of the role of vanadium in living systems.

In the present work, chromatographic experiments on citrate and lactate systems were carried out to elucidate the isotope effects in vanadium complexation. We also intend to evaluate the better system for isotope ^{50}V enrichment through the calculation of the height equivalent to a theoretical plate (HETP) and slope coefficient *k*.

2. Experimental

2.1. Apparatus and reagents

The apparatus used for the chromatography for vanadium isotope separation is described schematically in Fig. 1. It consists of two ion-exchange columns with water jackets (100 cm×1.0 cm I.D., made of pressure-resistant Pyrex glass). A high-pressure pump was used for controlling the feeding solution at a constant flow-rate. To monitor the column pressure, a pressure gauge with a safety device was placed between the column and the pump. Flexible PTFE tubing of 0.8 mm I.D. was used to connect the columns, valves and pumps. The temperature was set at 298 K throughout the experiments by circulating the thermostated water through the jackets of the columns. A fraction collector is used for collecting the effluent emerging from the bottom of the column.

The ion-exchange resin used in the present work was SQS-6, a strongly acidic cation-exchange resin (70–90 μm, highly porous type) supplied by Asahi Chemical Industry. Eluting agents of 0.1 mol/dm^3 citric acid (COOH CH_2–COHCOOH–CH_2COOH) and lactic acid (CH_2OH–COOH) were adjusted to pH 7.2 and 7.0, respectively, with $NH_3 \cdot H_2O$ solution. All reagents were of analytical grade, purchased from Wako, and used without further purification.

2.2. Chromatographic method

The cation-exchange resin packed in the column was conditioned with 2 mol/dm^3 HCl solution to remove the impurities and to convert its ion form completely to the H^+ form, and then washed thoroughly with redistilled water. A measured volume of the 0.2 mol/dm^3 $VOSO_4$+0.1 mol/dm^3 H_2SO_4 solution was fed into the column to form the VO^{2+} adsorption band of suitable length (30 cm), which is a visible, dark cyan, in contrast with the orange yellow resin of the H^+ form. The eluting solution of 0.1 mol/dm^3 ammonium carboxylate was introduced into the top of the column to develop the VO^{2+} band. In the present work, the eluting agents used were ammonium carboxylates of citrate and lactate. The

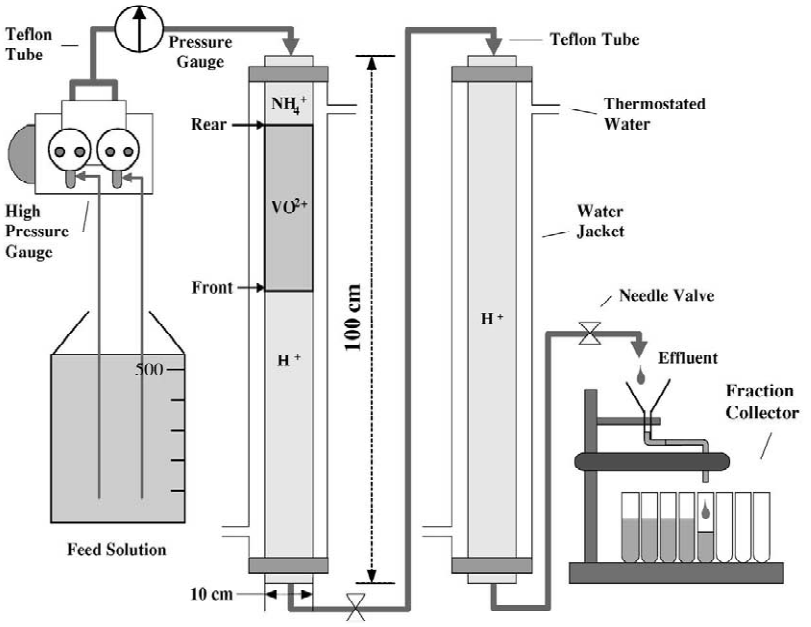

Fig. 1. Schematic separation system by displacement chromatography.

effluents collected in small fractions were applied to the analyses of pH, vanadium concentration and the isotope abundance ratio. The experimental conditions of these two systems are shown in Table 1.

2.3. Analysis

The vanadium concentration and the pH value in each fraction were determined by using an inductively coupled plasma atomic emission spectrometry (ICP-AES) system and pH meter. The determination of $^{50}V/^{51}V$ vanadium isotope ratios was carried out using a single-focusing magnetic sector field, Finnigan MAT 261 mass spectrometer, equipped with a thermal-ionization ion source and a Faraday cup collector for detection of the V^+ ion currents.

Prior to mass spectrometric analysis, the samples were pretreated. A portion of each sample fraction from the vanadyl carboxylate systems was treated with two acids. First, it was treated with concentrated nitric acid and evaporated to dryness on a hot plate to decompose the organic material. In these processes, VO^{2+} ions were partly oxidized to V_2O_5. Then these samples were reduced by the addition of concentrated hydrochloric acid and a deep blue aqua

Table 1
Selected experimental conditions of ligand-exchange chromatography

Complex system	VO–citrate	VO–lactate
Eluting agent	$(NH_4)_3$–citrate (0.1 mol/dm^3, pH 7.2)	NH_4–lactate (0.1 mol/dm^3, pH 7.0)
Temperature (K)	298±1	298±1
Feed solution	0.2 *M* $VOSO_4$+0.1 *M* H_2SO_4	0.2 *M* $VOSO_4$+0.1 *M* H_2SO_4
Migration length (cm)	199	199
Bed size (cm)	200 (length)×1.0 (I.D.)	200 (length)×1.0 (I.D.)
Flow-rate (cm^3/h)	5.7	4.7
Band velocity (cm/h)	1.5	0.4

Note: resin: highly porous type, strongly acidic cation ion-exchange resin (Asahi SQS-6, ~70 μm). Lactate: $CH_3CH(OH)COO^-$. Citrate: $CH_2(COO^-)(OH)C(COO^-)CH_2(COO^-)$.

solution was obtained. The sample was adjusted approximately to 0.5 mol/dm^3 vanadyl chloride solutions. From the prepared solution, a drop of 1 μl containing 20~30 μg vanadium is loaded onto the center of the cleaned evaporation filament and dried electrothermally.

When measuring the two vanadium isotopes ^{50}V and ^{51}V, isobaric interferences can occur with ^{50}Cr and ^{50}Ti. We found that the interference of ^{50}Ti was negligible, but in all cases, correction for ^{50}Cr was necessary. Chromium was always found to exist in the rhenium filaments of mass spectrometer, so scanning were made over the mass range from 50 to 52 to rigorously correct the possible interference by ^{52}Cr to ^{50}V peak. The ^{50}Cr peak height was calculated by measuring the peak height of ^{52}Cr.

The measurement was started 1.5 h from the beginning of the filament heating and continued for 1 h. The mass scanning over the mass range of 50 and 52 was repeated about 48 times. The vanadium isotope ratios were calculated by averaging all the height ratios of the recorded peaks of ^{50}V and ^{51}V. The total time for the mass spectrometric measurement of one sample was 2.5 h.

3. Results and discussion

3.1. Determination of equilibrium isotope effects by cation-exchange chromatography

Figs. 2 and 3 show the results obtained from the present chromatography experiments. These figures depict the ion-exchange chromatograms along with the changes in the pH values and the isotope abundance ratios for vanadyl–citrate and vanadyl–lactate systems, respectively.

Taking lactate as an example, the relative chemical reactions, which occur in the ion-exchange column, can be expressed as follows, at the rear boundary of vanadyl ions band:

$$\overline{VO^{2+}} + 2NH_4^+ + 2L^- \Leftrightarrow \overline{2NH_4^+} + VOL_2 \quad (1)$$

at the frontal boundary of vanadyl ions band:

$$VOL_2 + \overline{2H^+} \Leftrightarrow 2HL + \overline{VO^{2+}} \quad (2)$$

where the ‘‘—’’ denotes the resin phase and L^- stands for the lactate ligand. According to the physico-chemical properties of the large stability constants of vanadyl carboxylate complexes and the dissociation constants of corresponding carboxylic acids [16], the above two reactions tend to proceed to the right hand sides. Thus, the vanadyl carboxylate

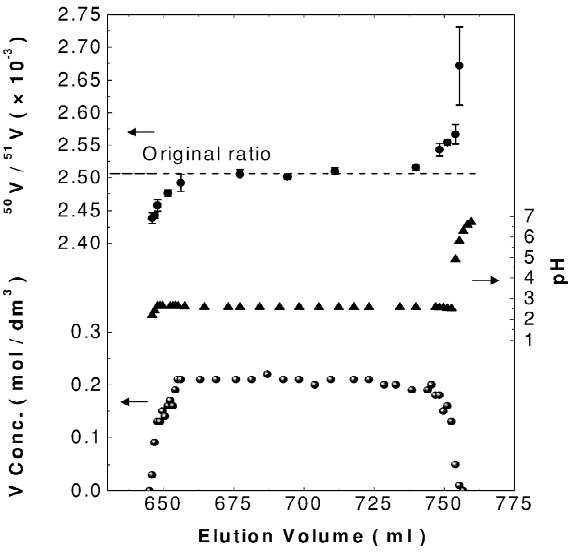

Fig. 2. Chromatogram and isotope ratios for the vanadyl citrate system.

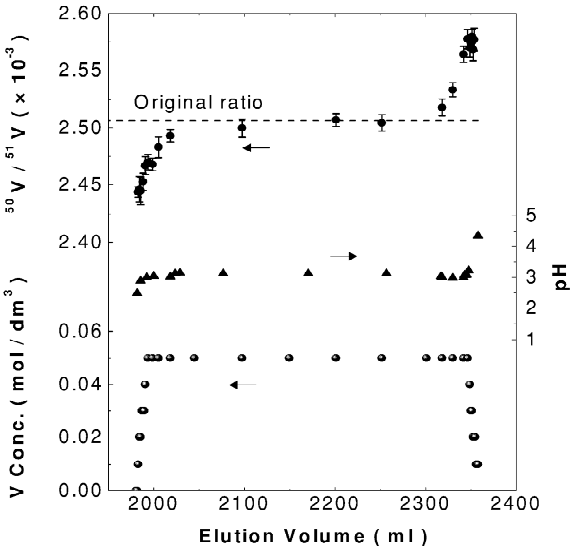

Fig. 3. Chromatogram and isotope ratios for the vanadyl lactate system.

complexes are eluted from the resin down to the bottom of the adsorption band successively. At the front boundary, the vanadyl complex is dissociated again and vanadyl ion is adsorbed into the resin. As a consequence of these processes the vanadyl ion band migrates down through the column with sharp boundaries at the both edges of the vanadyl ion band. It is obvious from the features of isotopic ratio illustrated in Figs. 2 and 3 that the heavier isotope ^{51}V are enriched in the vanadyl carboxylate complexes, which are the same tendency as the one in the previously studied malate system. These results suggest that the equilibrium constant of the following isotope exchange reaction should be larger than unity in each system of interest:

$$\overline{^{51}VO^{2+}} + {}^{50}VOL_2 \Leftrightarrow \overline{^{50}VO^{2+}} + VOL_2 \quad (3)$$

The isotope effect is evaluated as the elemental separation coefficient ϵ:

$$\epsilon = \alpha - 1 = \frac{[^{50}V/^{51}V]_r}{[^{50}V/^{51}V]_s} - 1 \quad (4)$$

where α refers to the isotope fractionation factor, or the single stage separation factor; the brackets denote the abundance ratio of given isotopes, and the subscripts r and s represent the resin and solution phases, respectively. The isotopes and phases in the numerator and the denominator in Eq. (4) were chosen to give the value of α larger than unity.

The separation coefficients ϵ are calculated from the present experimental data using the isotopic enrichment curves of the front or rear boundary according to the equation developed by Spedding et al. [17] and Kakihana and Kanaki [18] as $2.21 \cdot 10^{-4}$ and $2.45 \cdot 10^{-4}$ for the citrate and lactate systems, respectively. The calculating process was mentioned in the previous work.

Table 2 lists the separation coefficients ϵ of the vanadyl–carboxylate systems observed by a chromatographic method including the previously obtained ϵ of the malate system. Table 2 also lists the previously reported results of UO^{2+} [4] ions in the same carboxylate ligand exchange systems. It is very interesting that the order of the magnitude is opposite between the separation coefficients of vanadyl ions and uranyl ions. It was reported that the results of the uranyl citrate, uranyl malate, and uranyl tartrate systems bring out a striking similarity, viz. in each of these systems the complex species formed in solution in the pH range 2–4 is predominantly binuclear, in which bridging between metal ions occurs through carboxylate and hydroxyl groups of the ligand. And the dimerization constants (K_d) follow the order of citrate>malate>tartrate [19,20]. However in the uranyl lactate system, no binuclear complex formed [21]. Therefore, in uranyl carboxylate complex systems the existence of binuclear UO_2^{2+} complexes may create the conditions for larger isotope fractionation, for the separation coefficients follow the order malate>citrate=tartrate>lactate [7,8].

Table 2
Separation coefficients ϵ of VO^{2+} and UO_2^{2+} for carboxylate complex systems*

MO^{2+}	Isotope pair	ϵ ($\cdot 10^{-4}$) ($\epsilon=\alpha-1$)		
		Malate	Citrate	Lactate
VO^{2+}	$^{50}V/^{51}V$	1.0	2.2	2.4
UO^{2+}	$^{235}U/^{238}U$	−2.2	−1.8	−1.4

*: ϵ were calculated by the use of experimental data for enrichment zone. Definitions of ϵ for vanadyl and uranyl systems, respectively, are as follows:

$$\alpha = \frac{[^{50}V/^{51}V]_{resin}}{[^{50}V/^{51}V]_{complex}} = 1 + \epsilon \qquad \alpha = \frac{[^{235}U/^{238}U]_{resin}}{[^{235}U/^{238}U]_{complex}}$$

On the contrary, the separation coefficients of vanadyl carboxylate systems follow the inverse order lactate>citrate>>malate. It is known that also at low pH range the mononuclear and binuclear complexes coexist in vanadyl citrate [22,23], but only mononuclear species exist in the malate system [24] in the pH range concerned. The existence of binuclear complexes is probably the reason why the separation coefficient ϵ in the citrate system is much larger than that in the malate system. In the case of the lactate system, from electron spin resonance (ESR) [25], for (*R*)-lactic acid (H_2lact), five species were required: $[VO(Hlact)]^+$, $[VO(Hlact)_2]_2$, [VO(lact)], $[VO(lact)(Hlact)]^-$, and $[VO(Hlact)_2]^{2-}$, of which one species is in the form of a binuclear species $[VO(Hlact)_2]_2$. In addition, according to UV–Vis spectrometry carried out by Micera et al., in the bis-chelated complex the ligands have a *trans*-arrangement and the geometry at vanadium may exhibit a distortion toward the trigonal bipyramid

[26]. It is difficult to explain the larger separation coefficient obtained in the lactate system according to available knowledge. However, if the existence of binuclear complexes can result in the conditions for larger isotope fractionation, we can speculate there might exist predominantly binuclear species in the lactate complex in acidic solution or the large isotope effect may also attribute to the distortion in vanadyl complex. Thus, we anticipate that the isotopic effects will be a fresh source of information for the coordination chemistry of transition metals in solutions.

3.2. Calculation of HETP (height equivalent to a theoretical plate)—isotope accumulation processes

In order to evaluate the performance of the vanadium fractionation in displacement chromatography, HETP, the height equivalent to a theoretical plate is introduced. In a transient state, as in the case of the present work, HETP is determined using the following convenient equations proposed by Fujii et al. [27]:

$$\mathrm{HETP} = \frac{\epsilon}{\kappa} \cdot \left[1 + \frac{R_o}{\exp(\epsilon\kappa R_o L) - 1} \right] \quad (5)$$

When the enrichment extent is not so large, i.e., $\epsilon\kappa R_o L << 1$:

$$\mathrm{HETP} = \frac{\epsilon}{\kappa} + \frac{1}{\kappa^2 L} \quad (6)$$

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:

$$\ln(r_i - r_o) = \kappa(L - x) \quad (7)$$

In Eqs. (5)–(7), HETP is the height equivalent to a theoretical plate; κ the slope coefficient, R the isotope atom fraction, $r(=R/1-R)$ the isotope ratio, L the migration distance of the adsorption band boundary, x the distance from the starting point of the migration. 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 Fig. 4, from which κ can be obtained.

Like separation factor, slope coefficient κ, is also an important process parameter, which governs the shape of the isotope accumulation curve and thus determines the necessary inventory and the time required to obtain the product with the desired degree of enrichment. The value of the slope coefficient κ becomes smaller with the progress of the chromatographic operation [28].

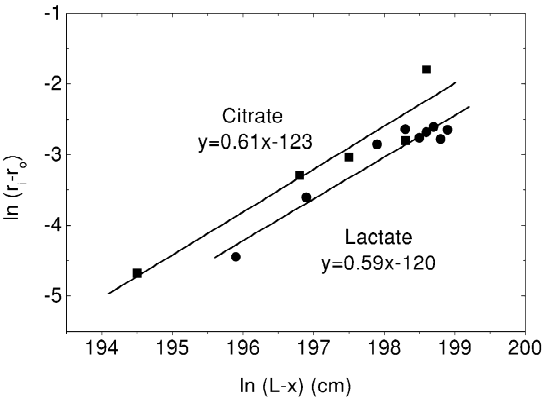

Fig. 4. The slope analysis of isotope enrichment in vanadyl adsorption band in citrate and lactate systems. y represents the slope equations of the rear parts of the chromatograms (■: citrate; ●: lactate).

The observed separation coefficient ϵ, the height equivalent to a theoretical plate HETP and the slope coefficient κ in the rear boundary of each system in this work are collected in Table 3, along with the operating time and the eluent volume used. The results in this table indicate, that ϵ decreases in the order lactate>citrate>malate, whereas the κ value is hardly affected by the ligand, having the values of about 0.59 and 0.61 for the systems studied. With increasing κ, the isotopic fraction profile of the isotope enrichment zone shows a sharp increase, and thus the width of the enrichment zone diminishes and the degree of accumulation of ^{50}V at the rear part of the zone increases. In addition, when the enrichment zone is narrow, one can form a narrow band of the

Table 3
Results of ligand-exchange chromatography

Complex system	VO–lactate	VO–citrate
Displacement time (h)	506	132
Total eluent volume (ml)	2360	758
Separation coefficient, ϵ	2.4×10^{-4}	2.2×10^{-4}
Slope coefficient, κ	0.59	0.61
HETP (mm)	0.15	0.14

isotope mixture in the column, and hence increase the degree of the utilization of the column. The HETPs of lactate and citrate were calculated as 0.15 and 0.14 mm, respectively. The HETP value is very small in each system indicating that the vanadium bands were eluted in a satisfactory displacement manner with very sharp band boundaries at the edges of the bands, due to the homogeneous, small and highly porous resin used. Accordingly, the isotope exchange reaction rate is sufficiently large and the rate-determining step may be in the phase transfer process between the ion-exchange resin and the aqueous solution. We can use the HETP value and the separation factor to design the height of the separation tower for attaining our desired abundance ratio of ^{50}V. Considering the operating time and the exhausted volume amount of eluent, the citrate system may be better than the other tested systems for the isotope separation of vanadium by cation-exchange chromatography.

4. Conclusions

Isotope fractionations between vanadyl carboxylate complex in aqueous solution and vanadyl ions in cation-exchange resin were experimentally observed by ion-exchange displacement chromatography. After examination of the results in the citrate and lactate systems, as well as in the previously studied malate system, the following conclusions can be drawn.

(1) The vanadium bands were developed in a satisfactory displacement manner with very sharp band boundaries at the edges of the bands.

(2) The heavier isotope ^{51}V was enriched at the front boundary of vanadyl ion adsorption band in each system, the lighter isotope ^{50}V at the rear boundary, in accordance with the malate system.

(3) Although vanadyl ions have some similarity to the uranyl ions due to their having double bond of metal–oxygen, the enrichment direction of vanadium isotopes is opposite to that of the uranium isotopes.

(4) The separation coefficients obtained were $2.2\cdot 10^{-4}$ and $2.4\cdot 10^{-4}$ for citrate and lactate systems respectively, which are much larger than $1.0\cdot 10^{-4}$ obtained for the malate system.

(5) The magnitude of the separation coefficient for vanadyl malate, citrate and lactate complexes is in reverse order to the one observed for the same uranyl complex systems.

(6) The observed HETPs in the citrate and lactate systems are 0.14 and 0. 15 mm, and the corresponding slope coefficients κ are 0.61 and 0.59, respectively.

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