Fractionation of potassium isotopes in cation-exchange chromatography

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ABSTRACT

Ion-exchange chromatography of potassium was carried out to study the potassium isotope effect in aqueous ion-exchange systems. The heavier isotope, ^{41}K, was found to be preferentially fractionated into the resin phase. This trend was independent of the type of cation-exchange resin (strongly or weakly acidic), the kind of potassium salt (chloride or lactate), the kind of replacement ion for K^+ (Ca^{2+} or Sr^{2+}) and the operating temperature (25 or 70°C). The values of the single-stage separation factor minus 1 obtained were $1.25 \cdot 10^{-5} – 3.48 \cdot 10^{-5}$. It was inferred that the ion association in the resin phase increases the separation factor and that in the solution phase decreases it.

INTRODUCTION

The use of ion-exchange chromatography for isotope separations of metals was first attempted by Taylor and Urey [1] in 1938. Since then, there has been and still is a continuing interest not only in investigating basic isotope effects observed in ion-exchange reactions but also in finding practical chemical chromatographic methods for isotope separation based on the effects. Elements whose isotope separation by ion-exchange chromatography has been studied include lithium [2], boron [3], carbon [4], nitrogen [5], magnesium [6], sulphur [7], calcium [8], zirconium [9] and uranium [10].

In previous papers [11,12], we reported the results of the chromatographic separation of rubidium isotopes. The heavier isotope, ^{87}Rb, was retained more strongly than ^{85}Rb by cation-exchange resins, and this tendency was independent of the type of resin, the kind of rubidium salt and the operating temperature, within the experimental conditions studied. On the other hand, it has been reported by other workers [2] that with lithium isotopes, the heavier isotope, ^7Li, was preferentially

TABLE I

EXPERIMENTAL CONDITIONS AND LOCAL ENRICHMENT FACTOR AND SINGLE-STAGE SEPARATION FACTOR VALUES OBTAINED

Parameter	Run No.					
	K01	K02	K03	K04	K05	K06
Cation-exchange resin	Strongly acidic	Strongly acidic	Weakly acidic	Strongly acidic	Strongly acidic	Weakly acidic
Temperature (°C)	25.0 ± 0.2	25.0 ± 0.2	25.0 ± 0.2	25.0 ± 0.2	70.0 ± 0.2	70.0 ± 0.2
Resin bed height (cm)	410.7	404.5	202.5	408.6	405.0	200.4
Operating manner	Reverse	Band	Reverse	Reverse	Band	Reverse
[band length (cm)]	breakthrough	(25.0)	breakthrough	breakthrough	(30.8)	breakthrough
Potassium feed solution[a]	0.101 M KCl	0.104 M KL	0.102 M KCl	0.101 M KCl	0.103 M KL	0.108 M KCl
Eluent[a]	0.049 M CaCl$_2$	0.050 M CaL$_2$	0.050 M CaCl$_2$	0.052 M SrCl$_2$	0.051 M SrL$_2$	0.048 M SrCl$_2$
Flow-rate (cm^3 cm^{-2} h^{-1})	11.51	9.87	13.72	10.65	11.34	11.03
(cm^3 h^{-1})	(9.04)	(7.75)	(10.77)	(8.36)	(8.90)	(8.66)
Band velocity (cm^{-1})	1.01	0.87	0.89	0.97	1.06	0.72
R_{local}^{max}	1.0085	1.0065	1.0097	1.0092	1.0027	1.0039
R_{local}^{min}	—	0.9953	—	—	0.9954	—
$10^5 \varepsilon$	2.52	2.35[b]	3.48	2.52	1.25[c]	2.49

[a] L = lactate.
[b] Average of values from the front part ($2.64 \cdot 10^{-5}$) and the rear part ($2.07 \cdot 10^{-5}$) of the band.
[c] Average of values from the front part ($1.33 \cdot 10^{-5}$) and the rear part ($1.16 \cdot 10^{-5}$) of the band.

fractionated into the solution phase, *i.e.* the direction of the isotope effect in ion-exchange chromatography for lithium is the opposite of that for rubidium. It is therefore of interest to investigate whether the potassium isotope effect in ion-exchange chromatography is similar to that of rubidium or that of lithium. To clarify this point, we carried out a series of chromatographic experiments on potassium isotope separation. In this paper, we report the results of such experiments and analyse them on the basis of a theory on isotope distribution between two phases [13,14]. Naturally occurring potassium consists of two stable isotopes, ^{39}K (93.2581 atom% [15]) and ^{41}K (6.7302%), and a radioactive isotope, ^{40}K (0.0117%), the half-life of which is $1.24 \cdot 10^9$ years.

To the best of our knowledge, the only previous work on potassium isotope fractionation under aqueous ion-exchange conditions was that by Taylor and Urey [1]. They used zeolites as ion exchangers and reported that the heavier isotope, ^{41}K, was preferentially fractionated in the exchanger phase. Unfortunately, no value of the single-stage separation factor, S, was given. This paper is the first to report S values for potassium isotopes in aqueous ion-exchange systems. For mixed solvent systems, Schmidhalter and Schumacher [16] reported the potassium isotope effect between K^+ and KL^+, where L is a macrocyclic polyether. Using an elution chromatographic technique, they obtained S values of 1.00074–1.00118. In their systems, ^{41}K was enriched in the complex species.

Although obtaining exact magnitudes of isotope effects under aqueous conditions provides fundamental data for chemical isotope separation practice, its significance is of course not limited to that field of science. For instances, isotope effects could be used for elucidating geochemical cycles and interactions [17,18] and for understanding the hydration states of metal ions in aqueous solutions [19].

EXPERIMENTAL

Reagents

The ion-exchange resins used were a highly porous, strongly acidic cation-exchange resin, Asahi LS-6 (100–200 mesh), and a porous, weakly acidic cation-exchange resin, Diaion WK-13 (65–170 mesh). All reagents were of analytical-reagent grade and were used without further purification.

Chromatographic process

Six chromatographic experiments were carried out, four with the strongly acidic and two with the weakly acidic cation-exchange resin. The experimental conditions are summarized in Table I. In the experiments with the strongly acidic resin, two Pyrex glass chromatographic columns (210 cm × 1 cm I.D.) with water-jackets were connected in series with a PTFE tube (1 mm I.D.) so that the total resin bed height was *ca.* 400 cm, whereas in the experiments with the weakly acidic resin, only one column was used. Chromatography was operated either in a band displacement manner or in a reverse breakthrough manner; the chromatographic procedure in this work is basically the same used previously [12] except that Sr^{2+} in addition to Ca^{2+} was used as the displacement ion for K^+. The effluent from the columns was collected and portioned into fractions of 5 cm^3.

Analysis

The potassium concentration in each fraction of the effluents was determined flame photometrically using a Daini Seikosha SAS-727 atomic absorption spectro-meter after appropriate dilution with pure water. For selected fractions of each experiment [mostly fractions near the end(s) of the potassium band], the $^{39}K/^{41}K$ isotopic ratios were measured, the procedure for which was briefly as follows.

For each fraction, an aliquot containing about $5 \cdot 10^{-5}$ mol of potassium was treated to prepare the sample for mass spectrometry. The aliquot was passed through a chromatographic column packed with an anion-exchange resin (Dowex 1-X8) in the OH^- form. To the effluent from the column, which was in fact an aqueous potassium hydroxide solution, was added hydriodic acid, yielding a potassium iodide solution. This solution was evaporated until the concentration of potassium iodide became about 0.05 M and was subjected to the $^{39}K/^{41}K$ isotopic ratio measurement. Only Teflon or polyethylene ware was used in the mass sample preparation in order to minimize potassium contamination.

The $^{39}K/^{41}K$ ratio of a mass sample was measured with the double-filament surface ionization technique using a Finnigan MAT 261 mass spectrometer. The filament unit for the $^{39}K/^{41}K$ measurement consisted of two filaments, one a vaporizing filament and the other an ionization filament, both being made of rhenium ribbon. A 1-μl volume of the mass sample was loaded on the vaporizing filament and dried. Ionization was performed by passing a heating electric current through the ionization filament. When the ion beam intensities of $^{39}K^+$ and $^{41}K^+$ became sufficiently high, about 1 h after initiation of heating, the ^{39}K and ^{41}K mass peaks were repeatedly recorded. The mass scanning was repeated eight times in a block and ten blocks were recorded as one measurement. The measuring time was about 1 h, hence the total time spent for one measurement was about 2 h. The $^{39}K/^4K$ ratio of a block was calculated by averaging all the peak-height ratios in the block and that of the mass sample was calculated as an average of the $^{39}K/^{41}K$ ratios of the ten blocks.

In the present work, no attempt was made to measure $^{40}K/^{39}K$ or $^{40}K/^{41}K$ isotopic ratio.

RESULTS AND DISCUSSION

Examples of chromatograms and ^7Li isotopic molar fractions obtained are shown in Figs. 1–3. Fig. 1 presents the analytical results of run K01 using the strongly acidic resin and operated in the reverse breakthrough manner, Fig. 2 those of run K02 using the same resin and operated in the band displacement manner and Fig. 3 those of run K03 using the weakly acidic resin and operated in the reverse breakthrough manner. In each figure, the solid step-like line shows the potassium concentration profile and the open circles the ^{41}K istopic molar fractions. It is clearly seen that the heavier isotope, ^{41}K, is enriched in the rear part of the chromatogram, that is, it is preferentially fractionated into the resin phase. This trend is also observed in all the other experiments conducted, and is the same as that observed for the rubidium isotopes [11,12]; it is independent of the type of cation-exchange resin (strongly acidic *vs.* weakly acidic; run K01 *vs.* K03), of the kind of anions in the solution phase (Cl^- *vs.* lactate ion; run K01 *vs.* K02), of the kind of replacement ion for K^+ (Ca^{2+} *vs.* Sr^{2+}; run K01 *vs.* K04) and of the operating temperature (25°C *vs.* 70°C; run K02 *vs.* K05 and run K03 *vs.* K06).
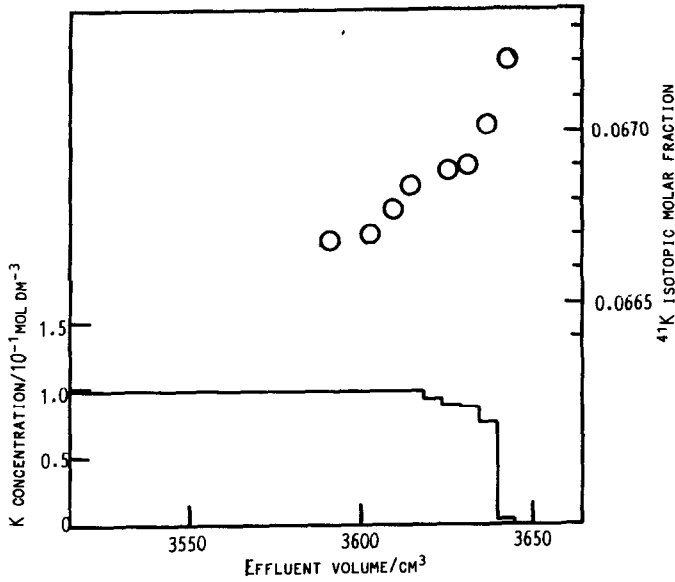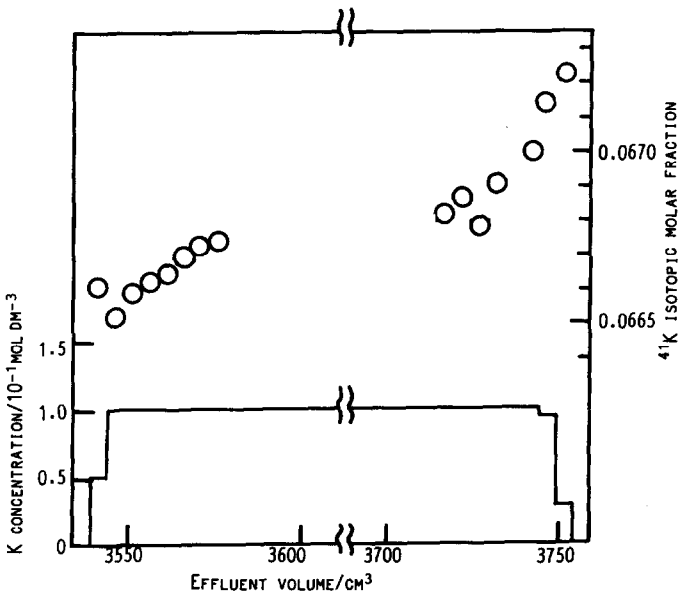
Fig. 1. Chromatogram and the ^{41}K isotopic molar fractions in run K01. Experimental conditions are summarized in Table I. The solid step-like line denotes the total potassium concentration and the open circles the ^{41}K isotopic molar fractions. The ^{41}K molar fraction of the feed solution is 0.06667.
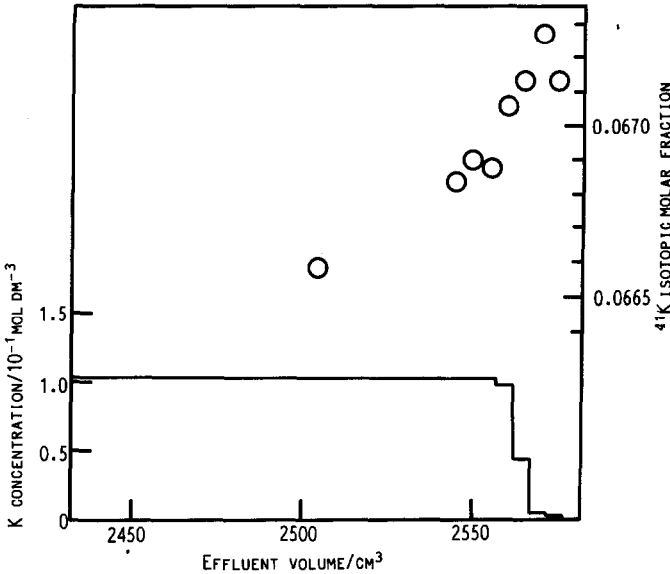

Fig. 2. Chromatogram and the ^{41}K isotopic molar fractions in run K02. Experimental conditions are summarized in Table I. The solid step-like line denotes the total potassium concentration and the open circles the ^{41}K isotopic molar fractions. The ^{41}K molar fraction of the feed solution is 0.06682.

Fig. 3. Chromatogram and the ^{41}K isotopic molar fractions in run K03. Experimental conditions are summarized in Table I. The solid step-like line denotes the total potassium concentration and the open circles the ^{41}K isotopic molar fractions. The ^{41}K molar fraction of the feed is 0.06667.

For each of the experiments, the maximum degrees of enrichment and/or depletion achieved expressed as the maximum and/or minimum of the local enrichment factor, R_{local}, defined as

$$R_{local} = ([^{41}K]/[^{39}K])_{fraction}/([^{41}K]/[^{39}K]_{feed} \qquad (1)$$

were calculated. In eqn. 1, [A] denotes the concentration of isotope A and the subscripts fraction and feed denote that the quantities refer to those of a fraction of the effluent and those of the feed solution, respectively. The results are given in Table I. R_{local}^{max} and R_{local}^{min} are the maximum degrees of enrichment and depletion, respectively. The highest R_{local}^{max} was achieved in run K03.

For each of the experiments, the single-stage separation factor, $S (= \varepsilon + 1)$, defined as

$$S = (\overline{[^{41}K]}/\overline{[^{39}K]})/([^{41}K]/[^{39}K]) \qquad (2)$$

where the quantities with overbars refer to those in the resin phase and the quantities without overbars to those in the solution phase, was calculated using the equation [20]

$$\varepsilon = \Sigma [| R_i - R_0 | f_i]/[R_0(1 - R_0)Q] \qquad (3)$$

where R_0 is the ^{41}K isotopic molar fraction in the feed solution, R_i that in the ith fraction, f_i the amount of potassium in the ith fraction, Q the total exchange capacity of

the resin for potassium and the summation is taken over all the fractions that are enriched or depleted in ^{41}K. The ε values obtained are listed in Table I; they are generally of the order of 10^{-5} and the maximum is obtained for the system with the weakly acidic cation-exchange resin at 25°C. The following may be deduced from a comparison of these values:

(1) In the systems with the strongly acidic resin, the magnitude of the potassium isotope effect depends on the kind of anions in the solution phase. Cl$^-$ yielded a larger ε value than the lactate ion (run K01 *vs.* K02).

(2) For the common potassium chloride feed solution, the weakly acidic cation-exchange resin (exchange group COO$^-$) gave a larger ε value than the strongly acidic resin (exchange group SO$_3^-$) (run K01 *vs.* K03).

(3) The potassium isotope effect in ion-exchange chromatography is independent of the kind of replacement ions for the K$^+$ (run K02 *vs.* K04), as is generally expected.

(4) The effect is temperature dependent, being larger at a lower temperature (run K02 *vs.* K05 and run K03 *vs.* K06).

These observations are qualitatively consistent with what had been observed for the rubidium isotopes [11,12], except for point (3), which was not examined for the rubidium isotopes.

In addition to the separation factor, parameters such as the HETP and the migration length required to obtain the desired degree of enrichment are essential in evaluating the feasibility of a certain chromatographic isotope enrichment system. These parameters are strongly dependent on such operating conditions as flow-rate, temperature and uniformity of packing. Unfortunately, the present experiments were not designed for obtaining values of the parameters with high accuracy; the migration lengths are too short and the maximum degrees of enrichment achieved are too low for this purpose, and a series of experiments in which only one of the experimental conditions is taken as a variable were not carried out. Although it is possible to evaluate the feasibility of the present systems based on theories of isotope separation by displacement chromatography [21,22], such an evaluation is merely an exercise in calculations and will convey no practical importance. In the following, we limit our discussion to the separation factors and extract information on fundamental potassium isotope effects underlying them.

Analysis of the observed potassium isotope effect on the basis of an isotope two-phase distribution theory

The theory of isotope distribution between two phases [13,14] correlates S with the isotopic reduced partition function ratios (RPFRs) and the molar fractions of the species in a separation system. An application of the theory to the present systems yields the following expression for S [12–14]:

$$\ln S = \ln S_{\text{phase}} + \ln \bar{S}_{\text{hydra}} + \ln [\bar{x} + (1 - \bar{x})\bar{S}_{\text{asso}}] - \ln [x + (1 - x)S_{\text{asso}}] \quad (4)$$

where

$$S_{\text{phase}} = \bar{f}_{\text{n},0}/f_{\text{n},0} \quad (5)$$

$$\bar{S}_{\text{hydra}} = \bar{f}_{\text{r},0}/\bar{f}_{\text{n},0} \quad (6)$$

$$S_{asso} = f_{n,1}/f_{n,0} \tag{7}$$

$$\bar{S}_{asso} = \bar{f}_{\bar{n},0}\bar{f}_{\bar{n},0} \tag{8}$$

and x and $\bar{x}$ are the molar fractions of the simple hydrated K^+ ion in the solution phase and in the resin phase, respectively. In eqns. 5–8, $f_{p,q}$ and $\bar{f}_{p,q}$ ($p = n$ or $\bar{n}$, $q = 0$ or 1) are the $^{41}K/^{39}K$ isotopic RPFRs of the species, $K^+(H_2O)_pL_q^-$, in the solution phase and in the resin phase, respectively, n and $\bar{n}$ the hydration numbers in the solution phase and in the resin phase, respectively, L^- the ion-association partner anion and q the number of anions ion-associated to a K^+.

S_{phase} is the separation factor due to the phase change, that is, the separation factor obtained when the simple hydrated species, $K^+(H_2O)_n$, is transferred from the solution phase to the resin phase without any change in the hydration circumstances. $\bar{S}_{hydra}$ is the separation factor originating from a change in the hydration number from n to $\bar{n}$ in the resin phase. It is usually considered that n is larger than $\bar{n}$ [23]. Therefore, ln $\bar{S}_{hydra}$ is negative. S_{asso} is the separation factor resulting from the ion association in the solution phase and $\bar{S}_{asso}$ is that in the resin phase.

In run K01, both the solution and the resin phases can be regarded as strong electrolyte solutions and no ion association is viable in either phase, i.e., $x = \bar{x} = 1$. Eqn. 4 is then simplified to

$$\ln S(K01) = \ln S_{phase}(K01) + \ln \bar{S}_{hydra}(K01) \tag{9}$$

ln $S(K01)$ is positive and ln $S_{hydra}(K01)$ is negative, so that ln $S_{phase}(K01)$ is positive, that is, the RPFR of the simple hydrated species is larger in the resin phase than in the solution phase, so the magnitude of ln $S_{phase}(K01)$ is larger than that of ln $S_{hydra}(K01)$.

In run K02, the situation in the resin phase is the same as that in run K01. In the solution phase, however, part of potassium ions are expected to be ion-associated with lactate ions. Thus, $\bar{x}$ is equal to unity but x is not. Eqn. 4 is simplified in this instance to

$$\begin{aligned}\ln S(K02) &= \ln S_{phase}(K01) + \ln \bar{S}_{hydra}(K01) - \ln [x + (1 - x)S_{asso}(K02)] \\ &= \ln S(K01) - \ln [x + (1 - x)S_{asso}(K02)]\end{aligned} \tag{10}$$

Substituting $2.52 \cdot 10^{-5}$ for ln $S(K01)$ and $2.35 \cdot 10^{-5}$ for ln $S(K02)$, we obtain $\ln[x + (1 - x)S_{asso}(K02)] = 0.17 \cdot 10^{-5}$. We have at present no estimate for the x value, but the value of ln $S_{asso}(K02)$ is evidentally at least $0.17 \cdot 10^{-5}$. A positive value of ln $S_{asso}(K02)$ means $f_{n,1} > f_{n,0}$, that is, the RPFR of the ion-associated species is larger than that of the simple hydrated species. Assuming that the effects of the hydration and the ion association on ln$f$ are additive, which is good as a first approximation, this result is reasonable and consistent with the formation of the outer-sphere ion-associated species. The fact that $S(K01)$ is larger than $S(K02)$ means that the ion association in the solution phase reduces the overall single-stage separation factor.

In run K03, the ion association between K^+ and COO^- is expected in the resin phase but not in the solution phase. A similar consideration to K02 yields the expression

$$\ln S(K03) = \ln S_{phase}(K03) + \ln \bar{S}_{hydra}(K03) + \ln [\bar{x} + (1 - \bar{x})\bar{S}_{asso}(K03)] \tag{11}$$

TABLE II

COMPARISON OF SINGLE-STAGE SEPARATION FACTOR VALUES BETWEEN POTASSIUM AND RUBIDIUM ISOTOPES AT 25°C

Heavier isotopes (^{41}K and ^{87}Rb) are preferentially fractionated into the resin phase.

Cation-exchange resin	Anion in solution phase	Ln S for	
		^{41}K/^{39}K	^{87}Rb/^{85}Rb
Strongly acidic	Cl$^-$	$2.52 \cdot 10^{-5}$	$5.2 \cdot 10^{-6}$
Strongly acidic	Lactate	$2.35 \cdot 10^{-5}$	$3.5 \cdot 10^{-6}$
Weakly acidic	Cl$^-$	$3.48 \cdot 10^{-5}$	$11.4 \cdot 10^{-6}$

Because of the difference in resin used in runs K01 and K03, $S_{phase}(K03)$ is not necessarily equal to $S_{phase}(K01)$ nor $\bar{S}_{hydra}(K03)$ to $\bar{S}_{hydra}(K01)$. However, it will not be a very poor approximation to put

$$\ln S_{phase}(K03) + \ln \bar{S}_{hydra}(K03) = \ln S_{phase}(K01) + \ln \bar{S}_{hydra}(K01) \qquad (12)$$

Assuming the equality in eqn. 12, we obtain $\ln [\bar{x} + (1 - \bar{x})\bar{S}_{asso}(K03)] = \ln S(K03) - \ln S(K01) = 3.48 \cdot 10^{-5} - 2.52 \cdot 10^{-5} = 0.94 \cdot 10^{-5}$. Like the x value in run K02, we have no estimate for the $\bar{x}$ value in this instance. Hence $0.94 \cdot 10^{-5}$ can be considered to be the possible minimum value of $\ln \bar{S}_{asso}(K03)$. A positive $\ln \bar{S}_{asso}(K03)$ value means that the RPFR of the ion-associated species is larger than that of the simple hydrated species in the resin phase. This result is reasonable in the light of the outer-sphere ion-associated species and is consistent with the result obtained in the previous paragraph. The fact that $S(K03)$ is larger than $S(K01)$ means that the ion association in the resin phase increases the overall separation factor.

The difference in replacement ion for K$^+$ is not included in eqn. 4, which explains why runs K01 and K04 give the same S value. This fact in turn indicates the high reliability of the S values obtained in this work.

TABLE III

COMPARISON OF VARIOUS S VALUES BETWEEN POTASSIUM AND RUBIDIUM ISOTOPES

For the definition of each kind of S, see the text.

Parameter	K	Rb
$\ln S_{phase}$:sign	+	+
$\ln \bar{S}_{hydra}$:sign	+	+
$\|S_{phase}\| > \|\bar{S}_{hydra}\|$?	Yes	Yes
$\ln S_{phase} + \ln \bar{S}_{hydra}$	$2.52 \cdot 10^{-5}$	$5.2 \cdot 10^{-6}$
$\ln S_{asso}$: sign	+	+
value (min.)	$0.17 \cdot 10^{-5}$	$1.7 \cdot 10^{-6}$
$\ln S_{asso}$: sign	+	+
value (min.)	$0.94 \cdot 10^{-5}$	$6.2 \cdot 10^{-6}$
S: temperature dependence	Normal	Normal

Comparison of potassium and rubidium isotope effects

Single-stage separation factor values obtained for the potassium and rubidium [11,12] isotope separation systems are compared in Table II. Information on various kinds of S for the two alkali metals, such as S_{phase} and S_{asso}, is summarized in Table III. These tables show that the signs of every corresponding isotope effect are the same, but that the magnitudes differ for the two metal ions. It is interesting to question whether such a correspondence can be extended to the light alkali metals, sodium and lithium. An answer to this will be given in a future paper.

CONCLUSION

Major findings of the present study are as follows.

(i) The heavier isotope, ^{41}K, was preferentially fractionated into the resin phase. This trend is independent of the type of cation-exchange resin (strongly acidic or weakly acidic), of the kind of potassium salts used in the feed solutions (potassium chloride or potassium lactate), of the kind of replacement ions for K^+ (Ca^{2+} or Sr^{2+}) and of the operating temperature (25 or 70°C).

(ii) The ε values were $2.52 \cdot 10^{-5}$, $2.35 \cdot 10^{-5}$ and $3.48 \cdot 10^{-5}$ for the potassium chloride–strongly acidic resin, potassium lactate–strongly acidic resin and potassium chloride–weakly acidic resin systems, respectively, at 25°C. The ε values for the second and third systems were $1.25 \cdot 10^{-5}$ and $2.49 \cdot 10^{-5}$, respectively, at 70°C. Thus, the potassium isotope separation effect showed the normal temperature dependence.

(iii) It was inferred that the ion association in the solution phase reduces the separation factor and that in the resin phase increases it, and that the RPFR value of the ion-associated species is larger than that of the simple hydrated species both in the solution phase and in the resin phase.

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