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Preliminary Results of the Studies on Fractionation of Ytterbium Isotopes in Yb(III)-Acetate/Yb-Amalgam System

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ABSTRACT

Preliminary data on the fractionation of ytterbium isotopes in a Yb(III)-acetate/Yb-amalgam exchange system were obtained. The light isotope was preferentially fractionated to the amalgam phase. The values of the unit separation gain per mass difference, ϵ, were found to be -0.00054 for $^{176/171}$Yb and -0.00069 for $^{176/174}$Yb. The difference, which amounted to 0.00015, may be taken as evidence for the occurrence of the so-called "even-odd" effect. It was also found that the chemical isotope shift of ytterbium was mirrored by the optical isotope shift in its atomic spectra.

INTRODUCTION

Studies on the fractionation of ytterbium isotopes in exchange systems were carried out in order to establish the relation between the chemical isotope effect and isotope masses.

The phenomenon called the "even-odd effect" or the "even-odd staggering of the isotopes" was first announced in 1989 by Fuji et al. (1) who found that in the red-ox exchange system of U(IV)–U(VI), the unit separation factor for the $^{238/235}$U isotope pair did not fit the linear interpolation between $^{238/234}$U

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and $^{238/236}U$. Nishisawa et al. observed the same difference in the behavior of even and odd isotopes of Sr and Ba (2), Zn (3), and Mg (4) in liquid–liquid extraction systems with dicyclohexano-18-crown-6 (DC18C6). The even-odd staggering of Gd isotopes was also announced by Nomura et al. (5) in cation-exchange displacement chromatography with EDTA and malonic acid as eluents with the reservation, however, that the measurement errors were too large to reach conclusions about the deviation from the theoretical relation of the mass dependence. Parallel unsuccessful attempts to find the even-odd effect in the fractionation of Sr (6) and Ba (7) by cation displacement chromatography have been reported.

For our studies we selected the rare earth ytterbium because of its interesting nuclear and chemical properties.. Naturally occurring abundance ratios of ytterbium isotopes are: ^{168}Yb (0.14%), ^{170}Yb (3.03%), ^{171}Yb (14.34%), ^{172}Yb (21.88%), ^{173}Yb (16.18%), ^{174}Yb (31.77%), ^{176}Yb (12.65%).

Ytterbium has five and two isotopes with even and odd mass numbers, respectively. The latter have different spin numbers ($I_{171} = 1/2$, $I_{173} = 5/2$) and different nuclear magnetic moment signs expressed in nuclear magnetons ($\mu_{171} = +0.49188$, $\mu_{171} = -0.67755$). Such a composition is rather unique.

From the chemical point of view, ytterbium belongs to a group of 14 rare-earth elements with the general electronic configuration of free atoms: $[Xe]4f^n5d^06s^2$. In the solution chemistry of Ln, a valence of 3+ with the configuration $[Xe]4f^{1-14}$ is typical. However, a few exceptions occur. Cerium forms stable Ce^{4+} ions, europium forms relatively stable Eu^{2+} ions, and ytterbium and samarium form much less stable Yb^{2+} and Sm^{2+} ions. The latter two, because of the very low value of the standard red-ox potential, $E(Yb^{3+/2+}) = -1.2$ V and $E(Sm^{3+/2+}) = -1.0$ V, are reoxidized by water itself or, according to Ref. 8, by H^+ ions with the evolution of hydrogen.

The instability of Yb(II) does not permit a study of the fractionation of its isotopes in red-ox exchange reactions which utilize countercurrent extraction or displacement chromatography as it was done for U(IV/VI) (1), Ce(III/IV) (9, 10), and Eu(II/III) (11).

Ytterbium, however, forms amalgams. This inspired us to develop a new separation process based on the reduction of Yb(III) by means of the sodium amalgam to produce the ytterbium amalgam Yb(Hg). The isotope effect in such system should reflect the three-electron exchange reaction: Yb(III) ↔ Yb(0).

EXPERIMENTAL

Reagents

Yb_2O_3 of purity grade 99.99 was supplied by Aldrich Chemical Co. The mean content of the isobars amounted to 20 ppm for Er and 3 ppm for Lu.

Acetate solutions of Yb^{+3} were obtained by dissolving the oxide in an excess of acetic acid: 3.5 M HAc/1 M Yb. The final pH of the 0.1 M $Yb(Ac)_3$ solution in 0.05 M HAc was about 4.5.

A sodium amalgam with a concentration of 2–3.5 M Na was prepared by dissolving sodium in mercury purified by digestion with a 5% $HgNO_3$ solution in 8% HNO_3, followed by washing with bi-distilled water and drying under vacuum. After dissolution, the Na amalgam was washed with xylene and absolute ethanol.

Analysis

Ytterbium was determined gravimetrically by oxalate precipitation and calcination at 850°C for 2 hours or by a spectrographic method using a Carl Ziess (Jena) spectrograph PGS-2.

The concentration of Yb(II) was determined by titration with 0.05 N $K_2Cr_2O_7$ using barium diphenyloamine sulfonate as indicator. Titration was performed in the presence of ferric ammonium sulfate, phosphoric acid, and sulfuric acid. The solution of reagents was deaerated by a stream of argon. Yb(II) was also determined spectrophotometrically using a Beckman DU 68 Spectrophotometer and 0.25 cm quartz cells.

The isotope ratios $^{176/171}Yb$ and $^{176/174}Yb$ were measured by means of a MAT 262 (Finnigan MAT) mass spectrometer. This instrument is equipped with 7 Faraday cup detectors. Six of them can be moved for optimal adjustment to selected masses. The method of total evaporation of the sample was applied. Thus, under normal conditions, there should be no mass fractionation effect (12).

Separation Process

The separation was performed in a 100-mL separation cell. At the beginning of the experiment the cell contained 50 mL of 0.1 M Yb(III) acetate solution and 260 g Hg. The content of the cell was strirred by means of a magnetic bar. The solution was deaerated with a stream of argon. The sodium amalgam, ~2.5 M Na(Hg), was then slowly pumped underneath the mercury surface by means of a peristaltic pump. The pH was controlled, and when it reached the proper value it was stabilized by the addition of acetic acid. At the end of the experiment the amalgam (A) and solution (S) phases were separated. The Yb(Hg) was washed with ethyl alcohol and etched with 4 M HCl for a few hours at 60°C in order to reextract ytterbium. Oxalates were then precipitated, and Yb_2O_3 was obtained by calcination at 850°C. The ytterbium oxides recovered from fractions A and S were used to obtain 0.1 M $Yb(Ac)_3$ solutions for the next separation stages.

The aim of the experiment was to extract 50% of the ytterbium from the initial solution to the ytterbium amalgam in a time as long as possible in order to establish isotope equilibrium.

In general, two competing reactions occurred in the studied chemical system.

1. Reduction of Yb(III) with the sodium amalgam to Yb(Hg) with Yb(II) as an intermediate stage:

$$Yb^{3+} + 3Na \rightarrow Yb^{2+} + 2Na + Na^{+} \rightarrow Yb^{0} + 3Na^{+} \quad (1)$$

2. Reoxidation and backextraction of ytterbium:

$$Yb^{0} + 3H_2O \rightarrow Yb^{2+} + H_2O + 2OH^{-} + H_2 \quad (2)$$
$$\rightarrow Yb^{3+} + 3OH^{-} + {}^{3}/_{2}H_2$$

as well as

$$Na + H_2O \rightarrow Na^{+} + OH^{-} + {}^{1}/_{2}H_2 \quad (3)$$

The rate of Reaction (1) depends mostly on the rate of delivering the Na(Hg) to the system. The rates of Reactions (2) and (3) depend on pH and on the kinds and concentrations of the ligand and counterions which influence the effective red-ox potential. Following literature suggestions (13–15), we chose acetates for our studies. However, citrates and ascorbic acid were also used in our preliminary experiments.

A series of experiments were performed to find the optimum conditions for our separation procedure. Some of them are presented in Table 1. For the given conditions a total time of 45 minutes and a final pH of 6.25, as in Experiment D-16, offer the best compromise. At higher pH, white hydrolysis products precipitate at the surface of mercury. At lower pH, the rate of reoxidation is probably too high to obtain Yb(Hg) of the desired concentration. After taking this into account, the conditions of Experiment D-16, slightly

TABLE 1
Separation Experiments: 50 mL, 0.1 M $Yb(Ac)_3$

	D-9	D-13	D-14	D-15	D-16	D-17	D-18
Concentration of Na in Na(Hg) (M)	1.28	1.39	3.68	2.31	3.9	2.84	2.44
Rate of Na addition (mmol Na/min)	0.47	0.48	0.57	0.58	0.41	0.38	0.21
Total time (minutes)	35	35	30	30	45	20	85
Final pH	7.25	7.03	6.55	6.2	6.25	5.48	6.25
Time of pH stabilization (minutes)	—	10	10	15	20	—	45
Extraction of Yb to Yb(Hg) (%)	<20	29	45	55	48	<5	14

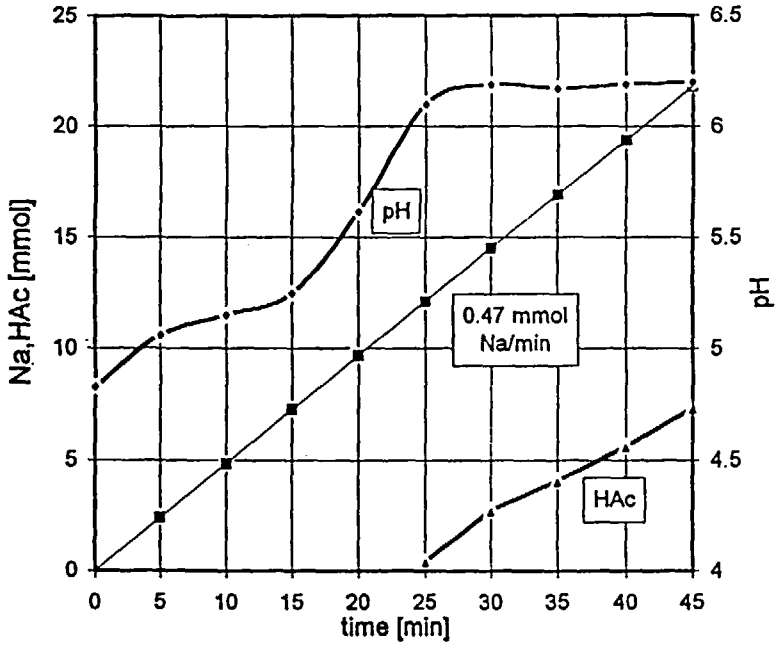

FIG. 1 Unit separation experiment.

modified, were adopted for cascade multiplication. The course of such an experiment, called "unit separation procedure, u.s.p.," is shown in Fig. 1. The final concentration of ytterbium in mercury was about 0.11% (by weight) or 0.078 M, and the molecular fraction of ytterbium in the amalgam, x_i, amounted to 0.0013.

Occurrence and Stability of Yb^{2+}

A deep yellow Yb(II) acetate appears upon addition of the first drops of Na-amalgam. The UV-Vis absorption spectra exhibit absorption bands at 252 and 351 nm, which is consistent with the literature data: 260 and 351 nm (16), 246 and 352 nm (17). The concentration of Yb(II) in the solution was determined by oxidimetry or by measurement of absorbance at 252 and 351 nm. The values of molar absorptivity calculated from oxidimetric and photometric data were $\epsilon_{252} = 920$ and $\epsilon_{351} = 479$.

It was estimated that the concentration of Yb(II) in the course of the experiment was 0.015–0.025 M for pH 5–6. The results, however, were not very precise because of the high rate of Yb(II) decay. The rate of its reoxidation

was determined by measuring changes in the absorbance at 252 and 351 nm. It was found that the reoxidation follows the first-order kinetic equation $\ln(C_0/C) = -kt$ with the rate constant $k = 0.09\ \text{min}^{-1}$ ($T_{1/2} = 8$ minutes).

Cascade Procedure

After phase separation the ytterbium was recovered and a pair of new stock solutions were prepared for the next stage of the separation procedure. To attain a 5-stage separation, a simple cascade procedure with two branches, solution (S) and amalgam (A), was applied. To preserve a constant concentration of ytterbium along the cascade, separation at the first stage was done by repeating u.s.p. 12 times in order to collect a sufficient amount of ytterbium for the next separation stages. At the second stage u.s.p. was repeated 6 times (3 in branch A and 3 in branch S). At the last stage the initial volume of the 0.1 M ytterbium solution had to be reduced to 10 mL.

The S and A fractions from the last separation stage were analyzed for the $^{176/171}$Yb and $^{176/174}$Yb isotope ratios (R). The results of the analysis are shown in Table 2, along with the calculated process separation factors (5 stages), Q; unit separation factors, $q = Q^{1/5}$; and unit separation gains divided by isotope mass difference, $\epsilon = (1/\Delta m) \ln q$. Each value of R and related RSD (relative standard deviation) were calculated from the analysis of two samples. The unit separation factor $q \pm$ SD (standard deviation) as a function of mass number is shown in Fig. 2.

DISCUSSION

It follows from the obtained data:

$$^{176/171}q_{A/S} = 0.99729; \qquad ^{176/171}\epsilon = -0.00054$$

$$^{176/174}q_{A/S} = 0.99863; \qquad ^{176/174}\epsilon = -0.00069$$

TABLE 2
Fractionation of Yb Isotopes in Amalgam/Acetate System

	R(176/171)		R(176/174)	
Phase		RSD (%)		RSD (%)
Amalgam	0.89261	0.024	0.40056	0.01
Solution	0.90480	0.087	0.40332	0.056
$Q_{A/S}$	0.98652	0.093	0.99316	0.055
$q_{A/S}$	0.99729	0.018	0.99863	0.01
$\epsilon = (1/\Delta m) \ln q$	−0.00054	6.7	−0.00069	7.4

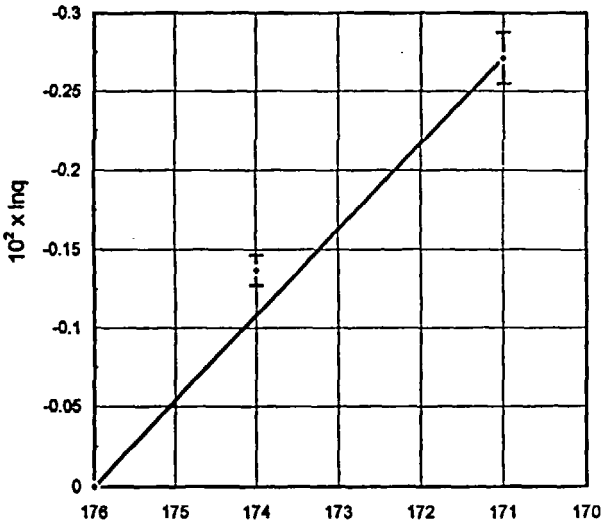

FIG. 2 Unit separation factor as a function of mass number.

that in the studied exchange system the light isotopes are preferentially fractionated to the amalgam phase. The separation factor q formally corresponds to the isotope equilibrium in the three or two electron exchange reactions presented by Reaction (1).

$$^{L}\text{Yb(Hg)} + {}^{H}\text{Yb(Ac)}_p^n \leftrightarrow {}^{L}\text{Yb(Hg)} + {}^{H}\text{Yb(Ac)}_p^n \qquad (4)$$

where L and H are the light and heavy isotopes, respectively, ${}^{H}\text{Yb(Ac)}_p^n$ represents Yb(II) or Yb(III) acetate complexes; and Yb(Hg) represents intermetallic compounds in the amalgam phase.

In the present state of the studies it is difficult to conclude which complex is mainly responsible for the isotope fractionation. Their composition is rather variable because the pH and concentration of sodium ions increase in the course of the experiment. The sequence of the red-ox reactions occurring in the chemical system is not exactly known; Reactions (1) and (2) represent a rather simplified picture. Direct reduction of Yb(III) to Yb, beside the two-step reduction, should also be taken into consideration. For example, no Yb(II) was observed (13) when amalgamation was performed by the falling drop method which provides a very short contact time.

The difference between the values of ${}^{176/171}\epsilon$ and ${}^{176/174}\epsilon$ (amounting to 0.00015) may be taken as evidence for the occurrence of the even-odd effect in ytterbium isotope fractionation. Thus ytterbium has become the first ele-

ment of the rare earth group and the sixth element of all elements that demonstrates such an effect.

It follows from the relation

$$|^{176/174}\epsilon| > |^{176/171}\epsilon|$$

that separation of the even-even isotope pair is more efficient (by a factor of 1.27) than separation of the even-odd pair. The opposite relation was observed in the fractionation of uranium isotopes (1). In the red-ox exchange systems U(VI) ↔ U(VI) and U(VI) ↔ U(III), it was found that the even-odd isotope pair was separated more efficiently (by a factor of 1.16) than the even-even isotope pair, according to

$$|^{238/236}\epsilon| = |^{238/234}\epsilon| = |-0.00037| < |-0.00043| = |^{238/235}\epsilon|$$

In general, considering the uranium fractionation data, it has been observed that a nucleus with an odd number of neutrons behaves in chemical reactions as though it has a smaller atomic mass. In fact, to normalize the uranium fractionation data in terms of mass dependence ($\ln q \approx \Delta m/m^2$), the value 234.5 should be used for ^{235}U whereas to normalize the ytterbium fractionation data the value 172 should be used for ^{171}Yb because the ytterbium isotope with an odd number of neutrons behaves in chemical reactions as though it has a higher atomic mass.

It is also interesting to note that similar differences in the behavior of ytterbium and uranium isotopes occur in their atomic spectra. For comparison, we have taken the changes in the nuclear charge radius, $\delta\langle r^2\rangle fm^2$, derived from field shift fraction in the total optical shift. The optical isotope shift of ytterbium is mostly due to the field shift; the mass shift can be neglected.

In fact, for uranium we have

$$[(1/2)\delta\langle r^2\rangle]_{238,236} = [(1/2)\delta\langle r^2\rangle]_{238,236} = 0.5 < 0.56 = [(1/3)\delta\langle r^2\rangle]_{238,235}$$

where $\delta\langle r^2\rangle$ is derived from the optical shift of the 5027 nm line by Gagné et al. (18) and based on the assumption: $[\delta\langle r^2\rangle]_{238.236} = 1$.

For ytterbium, the values of $\delta\langle r^2\rangle fm^2$, calculated by Stark et al. (19, Table 9.18) from the optical shift of the $\lambda_{555.6}$ nm line for the pure transition $4f^{14}6s^2\ {}^1S_0 - 4f^{14}6s6p\ {}^3P_1$ give the relation:

$$[(1/2)\delta\langle r^2\rangle]_{176,174} = |-0.0045| > |-0.0040| = [(1/5)\Sigma\ \delta\langle r^2\rangle]_{176,171}$$

where the value for 176/171 is the sum of $\delta\langle r^2\rangle$ values for three consecutive isotope pairs: 176/174, 174/172, 172/171.

Thus, our preliminary results confirm the resemblance between the chemical isotope shift in exchange reactions and the isotope field shift in atomic spectra, as first observed by Bigeleisen (20). The resemblance may be casual,

but it is in general agreement with recent theoretical discoveries (21) that others factors beside the classic mass effect have to be taken into account.

In our further studies, now in progress, we intend to obtain separation data for the others ytterbium isotope pairs as well as data on the separation of samarium isotopes in the amalgam/acetate system.

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