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Sublimation Behavior of Actinoid Chelates of 2,2,6,6-Tetramethyl-3,5-heptanedione

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Vacuum sublimation-recrystallizing temperatures were determined for a tracer amount of actinoid chelates of 2,2,6,6-tetramethyl-3,5-heptanedione in order to obtain information about their sublimation behavior. The influence of the amount of sample (in tracer scale or in milligram scale) on its sublimation-recrystallizing temperature was also examined. The sublimation-recrystallizing zone temperature of the tracer amount of chelate was lower than that of the milligram amount. In addition, the sublimation-recrystallizing zone temperatures of the actinoid chelates were found to be in the following sequence: UO_2^{2+}>Am(III), Cm(III)>Th(IV), Np(IV), Pu(IV)>Cf(III). These results suggest that the sublimation technique can be applied to separate the actinoid elements in a carrier-free state.

A number of workers have studied the volatility of lanthanoid β-diketone chelates. They reported that 2,2,6,6-tetramethyl-3,5-heptanedione makes a highly volatile and thermally stable lanthanoid chelate.[1-4] In previous work,[5,6] we have studied the sublimation behavior of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-lanthanoid(III) (La(III)(thd)$_3$) in detail, and have shown that the behavior can be divided into three groups (La to Gd, Tb and Dy, and Ho to Lu) and that the middle lanthanoid chelates (Tb and Dy) change thermally in solid phase at various fixed temperatures. Their volatilities have also been found to affect the two different crystallographic forms. It is therefore important to study the sublimation behavior of actinoid chelates of 2,2,6,6-tetramethyl-3,5-heptanedione. Among the actinoid metal chelates, uranyl(UO_2^{2+}) and thorium-(Th(IV)) chelates of β-diketone have already been examined as to volatility by using a milligram amount of sample.[7,8] Sakanoue and Amano have prepared some other actinoid β-diketonato chelates in tracer scale and described their volatilities.[9]

In the present study, in order to obtain the sublimation-recrystallizing temperatures of actinoid chelates of 2,2,6,6-tetramethyl-3,5-heptanedione, we examined the influence of sample amount (milligram amount or tracer amount) on their sublimation-recrystallizing temperatures. In addition, their sublimation behavior was determined for a tracer amount of actinoid chelates, and this was compared with those of lanthanoid chelates.

Experimental

Reagents. *Actinoid Metal*: Uranyl nitrate and thorium nitrate were purchased commercially in gram quantities, and used without delicate handling because of their low specific radioactivities. Other actinoid metals were used in tracer scale. Some actinoid radioisotopes: ^{227}Ac, ^{241}Am, ^{243}Am, and ^{242}Cm, were purchased from The Radiochemical Centre (England) and from New England Nuclear corporation (U. S. A.). The daughter nuclides, ^{228}Ac and ^{234}Th, were obtained by a milking procedure from the parent nuclides, ^{228}Ra and ^{238}U. Californium radioisotope, ^{252}Cf, was recovered from a nickel foil which had covered a ^{252}Cf neutron source; was obtained enough to prepared its chelate and determine its radioactivity. The plutonium radioisotope, ^{239}Pu, was obained by Inoue.[10] The radioactivities and metal amounts of actinoids used in preparation and their specific radioactivities are summarised in Table 1.

Table 1. Radioactivities, metal amounts, and specific activities of actionoid and gadolinium nuclides, which are used in one preparative procedure[a)]

Radio-nuclide	Radio-activity/μCi	Metal amount/mg	Specific activity/μCi mg^{-1}
^{228}Ac	10	4.5×10^{-9}	2.2×10^{9}
^{228}Th	5	6.1×10^{-6}	8.2×10^{5}
^{232}Th[b)]	3.3×10^{-2}	300	1.1×10^{-4}
^{234}Th	2	8.6×10^{-8}	2.3×10^{7}
^{238}U[b,c)]	1.0×10^{-1}	300	3.4×10^{-4}
^{239}Np	10	4.3×10^{-8}	2.3×10^{8}
^{239}Pu	1.0×10^{-2}	1.6×10^{-4}	6.2×10^{1}
^{241}Am	1	2.9×10^{-4}	3.4×10^{3}
^{242}Cm	2	6.0×10^{-7}	3.3×10^{6}
^{252}Cf	1.0×10^{-3}	1.9×10^{-3}	5.4×10^{-1}
^{153}Gd[d)]	5	2.2×10^{-3}	2.3×10^{3}

a) One-tenth of the amounts in this table was used in one sublimation procedure. b) Thorium and uranium are weighable. c) A depleted uranium sample was used. d) The purchased Gd radioisotope is not carrier-free, and contains other stable Gd isotopes.

Lanthanoid Carriers and Radioisotope: The purified lanthanoid oxides (99.9%) of La_2O_3, Gd_2O_3, and Sc_2O_3 were used as a carrier for the preparation of actinoid chelates in tracer scale. Gadolinium radioisotope, ^{153}Gd, were purchased from The Radiochemical Centre (England).

Preparation of Actinoid Chelates of 2,2,6,6-Tetramethyl-3,5-heptanedione. Macro amounts of thorium and uranyl chelates, Th(thd)$_4$ and UO_2(thd)$_2$·2H_2O, were prepared by mixing 90% methanol solutions of the neutralized 2,2,6,6-tetramethyl-3,5-heptanedione chelating agent and thorium nitrate or uranyl nitrate. The chelates precipitated immediately upon mixing the solutions and were purified by recrystallization from dichloromethane and vacuum sublimation. The purified uranyl chelate was found to be unhydrous form, UO_2(thd)$_2$, by elemental and thermochemical (TG, DTA) analyses.

Tracer amounts of other actinoid chelates of 2,2,6,6-tetramethyl-3,5-heptanedione were prepared according to the preparative method for Ln(thd)$_3$ (Ln=lanthanoid metal) of Eisentraut and Sievers[1] with a slight modification, by the use of about 100 mg of lanthanoid metal as a non-isotopic carrier. The mixed solution of the lanthanoid salt solution and tracer amounts of each actinoid metal were heated to dryness. The residue was dissolved in a minimum amount of 99% methanol, and the pH of the resultant solution was adjusted between 3 and 5 by dropwise addition of 2 M NH_4OH solution. A solution of Hthd chelating agent was then added to the above solution. The mixture was adjusted to the desired pH. The precipitate was filtered off and then purified by recrystallization from dichloromethane. Several sets of the chelates were prepared as follows: $(La+^{228}Th)(thd)_3$, $(La+^{234}Th)(thd)_3$, $(UO_2+^{234}Th)(thd)_2$, $(La+^{228}Ac+^{228}Th+^{239}Np+^{239}Pu+^{241}Am+^{252}Cf)(thd)_3$, $(UO_2+^{234}Th+^{239}Pu)(thd)_2$, $(La+^{153}Gd)(thd)_3$, $(Sc+^{153}Gd)(thd)_3$, and $(La+^{241}Am+^{242}Cm+^{252}Cf)(thd)_3$;

Measurements of Vacuum Sublimation-recrystallizing Temperatures. Specifications for the vacuum sublimation apparatus for the measurement of the vaccum sublimation-recrysrallizing temperature were reported in the previous paper.[6] Briefly, the apparatus consists of a Pyrex tube (0.8 cm in outer diameter and 100 cm in length) with a continuous temperature gradient (1—3 °C/cm) maintained along its length, and evacuated to (1—10)×10^{-3} Torr)(1 Torr≈133.322 Pa). Samples were placed in small aluminum or porcelain boat and inserted into the high temperature end of the Pyrex sublimation tube. The samples then heated at 180 °C for 2 h under reduced pressure ((1—10)×10^{-3} Torr)). Their recrystallizing positions were determined by the scanning of the radioactivity along the sublimation tubes.

Special care has been paid in comparing the recrystallizing position of each actinoid chelate. Two sublimation tubes were inserted in an outer tube to sublimate each sample under the same conditions. The small differences between the sublimation-recrystallizing temperatures of each sample were clearly detected.

Radioactivity Measurement. While the gross gamma and characteristic X-ray were measured with a well-type NaI(Tl) scintillation counter, the gamma ray spectra were taken by using a Ge(Li) semiconductor detector connected with a 4096-channel pulse-height analyzer. Alpha spectra were taken with a Si(Au) semiconductor detector coupled to a 4096-channel pulse-height analyzer. The detection of alpha particles was also done by an α-track method by using a cellulose nitrate film. The ^{252}Cf radioactivity was measured by using Indian mica as a fission track detector. Both track methods (α-track and fission track methods) were very useful for locating clearly the sublimation-recrystallized chelate.

Results and Discussion

Vacuum Sublimation-recrystallizing Temperatures of Tracer Amounts of Metal Chelates of 2,2,6,6-Tetramethyl-3,5-heptanedione. In general, vacuum sublimation-recrystallizing temperature zones for macro amounts of metal chelates (more than 5 mg) can be observed discretely and reproducibly at the higher temperature site of the deposition zone, while the tailing appears in its lower temperature site.[6] In this experiment, the influence of the amount of sample on its sublimation-recrystallizing temperature was examined by the use of $Gd(thd)_3$ and $Th(thd)_4$. Figures 1 and 2 show these results. The peak position of the recrystallizing temperature zone for tracer amounts of $Gd(thd)_3$ or $Th(thd)_4$ shifted to a temperature position lower than that of macro amounts of $Gd(thd)_3$ or $Th(thd)_4$. On the other hand, the recrystallizing range of tracer amounts of chelate was also found to be equal to those of macro amounts of chelate. The tracer amounts of the sublimated chelates were located in discrete and reproducible temperature ranges. These reasons allow the sublimation behavior of tracer amounts of actinoid thd chelates to be expressed conveniently in terms of the sublimation-recrystallizing temperature range.

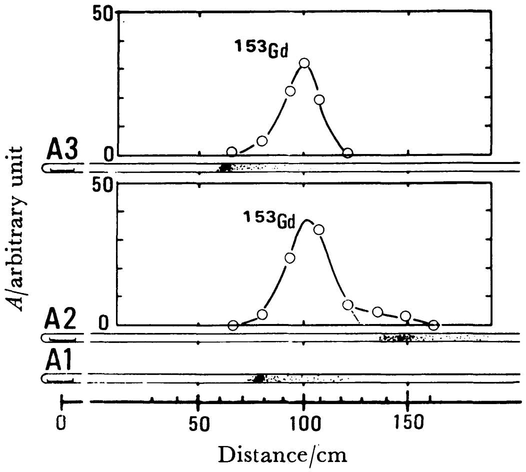

Fig. 1. Deposition zone and distribution of ^{153}Gd radioactivity along sublimation tube.
Sample, A1: $Gd(thd)_3$; A2: $(Sc+^{153}Gd)(thd)_3$; A3: $(La+^{153}Gd)(thd)_3$.

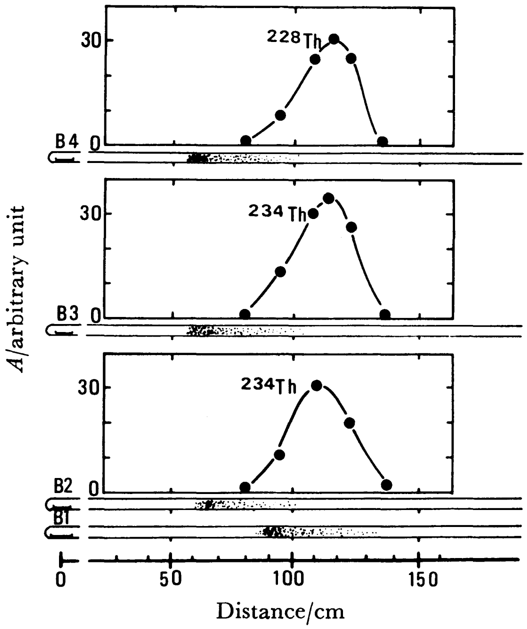

Fig. 2. Deposition zone and distribution of thorium radionuclide along sublimation tube.
Sample, B1: $Th(thd)_4$; B2: $(UO_2+^{234}Th)(thd)_2$; B3: $(La+^{234}Th)(thd)_3$; B4: $(La+^{228}Th)(thd)_3$.

Sublimation Behavior of Actinoid Chelates of 2,2,6,6-Tetramethyl-3,5-heptanedione. The shape of the sublimatographic distribution of each actinoid thd chelate was that of tracer amounts of $Gd(thd)_3$ and $Th(thd)_4$. The sublimation-recrystallizing temperatures for the various actinoid thd chelates are graphically presented and compared in Fig. 3. In this figure, the depositing

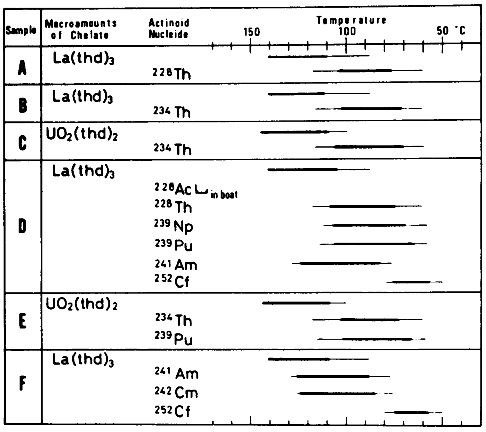

Fig. 3. Vacuum sublimation-recrystallizing temperature for tracer amounts of actinoid thd chelate.
Sample, A: $(La+{}^{228}Th)(thd)_3$; B: $(La+{}^{234}Th)(thd)_3$; C: $(UO_2+{}^{234}Th)(thd)_2$; D: $(La+{}^{228}Ac+{}^{228}Th+{}^{239}Np+{}^{239}Pu+{}^{241}Am+{}^{252}Cf)(thd)_3$; E: $(UO_2+{}^{234}Th+{}^{239}Pu)(thd)_2$; F: $(La+{}^{241}Am+{}^{242}Cm+{}^{252}Cf)(thd)_3$.

TABLE 2. VACUUM SUBLIMATION-RECRYSTALLIZING TEMPERATURE RANGES OF ACTINOID thd CHELATES

Actinoid thd chelate	Temperature range/°C
$Th(thd)_4$	60—118
$UO_2(thd)_2$	100—145
$Np(thd)_4$	59—113
$Pu(thd)_4$	59—115
$Am(thd)_3$	77—129
$Cm(thd)_3$	76—126
$Cf(thd)_3$	50—80

zones in a large portion(80%) of sublimated chelate are shown as a thicker line. Table 2 summarizes the sublimation-recrystallizing temperature ranges obtained for actinoid thd chelates. Many actinoid metals, The U, Np, Pu, Am, Cm, and Cf, made a highly volatile, and thermally stable chelate by using 2,2,6,6-tetramethyl-3,5-heptanedione chelating agent. However, Ac(III) thd chelate was not sublimed under the same sublimation conditions. The Ac(III) thd chelate will be unstable on heating.

It is difficult to estimate the valence state of tracer amounts of solid actinoid sublimates. The valence states of Am, Cm, and Cf ions in each starting solution were tervalent, and those of Th, Np, and Pu ions were quadrivalent. In general, valence states of Am, Np, and Pu ions tend to change in various solutions. Therefore special care was paid in each preparative step of these actinoid chelates. On the other hand, according to solvent extraction data of these actinoid chelates of β-diketone agents, β-diketonato chelates of Am(III), Np(IV), and Pu(IV) gives the highest values of formation constants in each actinoid β-diketonato chelates. In this experiment, the recrystallizing positions of these actinoid thd chelates were compared with those of other actinoid and lanthanoid chelates. Under these conditions, the coordination forms between the actinoid metals and the thd chelating ligands were estimated. The estimated chemical forms are shown in the first column in Table 2.

By comparing the above results, it is found that the sublimation-recrystallizing temperature range of actinoid thd chelates decreases in the following order:

$$UO_2(thd)_2 > \begin{matrix} Am(thd)_3 \\ Cm(thd)_3 \end{matrix} > \begin{matrix} Th((thd)_4 \\ Np(thd)_4 \\ Pu(thd)_4 \end{matrix} > Cf(thd)_3$$

The recrystallizing temperature ranges of tervalent $Am(thd)_3$, $Cm(thd)_3$ and $Cf(thd)_3$ were compared with those of the tervalent lanthanoid chelates, $Ln(thd)_3$. The recrystallizing temperature range of $Cf(III)(thd)_3$ was found to resembles those of the heavier lanthanoid (Ho–Lu) chelates, while the recrystallizing temperature ranges of $Am(III)(thd)_3$ and $Cm(III)(thd)_3$ chelates resemble those of the lighter lanthanoid (La, Pr–Gd) chelates.[5,6] Therefore the structures of the Am(III) and Cm(III) thd chelates should be different from that of the Cf(III)chelate. The Am(III) and Cm(III) thd chelates are estimated to be a dimer form, and the Cf(III) thd chelate may be a monomer form. As the dimer chemical forms of $Am_2(thd)_6$ and $Cm_2(thd)_6$ are improbable owing to very low metal concentrations, as shown in Table 1, $LaAm(thd)_6$ and $LaCm(thd)_6$ are possible forms.

The quadrivalent chelates of $Th(IV)(thd)_4$, $Np(IV)(thd)_4$, and $Pu(IV)(thd)_4$ recrystallized in a similar position of the sublimation tube. Since there are little difference in structure and molecular weight of $M(thd)_4$ (M=Th, Np, Pu), their van der Waals' forces will be equal and their sublimation behaviors would be similar. The recrystallizing temperature of $UO_2(thd)_2$ chelate was found to be higher than those of the other actinoid chelates. This sublimation behavior will be due to the structural characteristic of "nyl" ion.

The actinoid thd chelates gave a high thermal stability during sublimation, but showed a considerable difference in the sublimation-recrystallizing temperature. The differences of their sublimation behaviors may be due to the difference in vapor pressure, molecular weight, heats of sublimation, and surface area of these chelates. The differences in heats of sublimation can be regarded as significant, because the heats of sublimation are correlated with the space arrangement. However, a number of fundamental experiments must be undertaken in order to determine the sublimation behavior of tracer amounts of chelate compound.

The reproducibility of sublimation-recrystallizing temperatures suggests that the sublimation technique can be applied to separate the actinoid elements in a carrier-free state. It is proposed that the ^{238}U–^{234}Th, ^{243}Am–^{239}Np radioactive equilibrium mixture and the Am(Cm)-Cf mixture can be separated by a sublimation technique.

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