The Extractional Behavior of Cerium with Acetylacetone

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In previous papers[1,2] we have studied some details of the solvent extraction of cerium with acetylacetone—the conditions for the extraction, the interfering substances, and the application of the extraction technique to the separation of cerium-144 from the mixture of fission products.

In this paper we hope to make clear the extractional behavior of cerium in the form of the acetylacetonate. The oxidation number of cerium will be estimated, and the effects of the concentration of acetylacetone and temperature on the extraction will be studied.

Experimental

Reagents.—Commercial acetylacetone was purified by washing it with dilute ammonia water and then with distilled water, followed by distillation under the reduced pressure of 47 mmHg; the 56—57°C fraction was then collected. The purity of the product was checked by gas chromatography.

The carrier-free cerium-144 was imported from Amersham, England, in the form of cerous trichloride in a hydrochloric acid solution, which was dissolved in 2 N perchloric acid and then stored.

Benzene was purified by washing it with sulfuric acid and then with distilled water; it was then distilled.

The other chemicals used are all of a guaranteed reagent grade.

Distribution Measurements. — The distribution ratio of acetylacetone was determined as follows: A mixture of 5 ml. of an acetylacetone benzene solution of a known concentration and 5 ml. of an aqueous solution of 0.1 M sodium perchlorate at various pH values was mechanically shaken for 30 min. in order to attain the distribution equilibrium of acetylacetone at a regulated temperature. After the phases had settled, the volumes of the two phases, the concentration of acetylacetone and the pH in the aqueous phase were measured. The distribution ratio was defined as the ratio of the concentration of acetylacetone in the organic phase to the concentration in the aqueous phase.

The concentration of acetylacetone in the aqueous phase was determined by adding a large excess of an aqueous solution of ferric sulfate at pH 0.5 to an aliquot (1 ml.) of the sample solution, while the absorption at 650 mμ was measured by a spectrophotometer. The pH measurements were carried

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[1] N. Suzuki and S. Oki, This Bulletin, 35, 233 (1962).

[2] N. Suzuki and S. Oki, This Bulletin, ibid., 35, 273 (1962).

out within an accuracy of 0.01 pH unit with a glass electrode pH meter.

The distribution ratio of cerium was determined as follows: A mixture of 5 ml. of an acetylacetone benzene solution of a known concentration, which had extracted cerium at pH 6—7 beforehand, and 5 ml. of an aqueous solution of 0.1 M sodium perchlorate at various pH values was mechanically shaken for an hour in order to attain the distribution equilibrium at a regulated temperature. The initial concentration of cerium in the organic phase was the tracer concentration, the order of 10^{-9} M. After the phases had settled, an aliquot (1 ml.) was taken out from each phase into each polyethylene test tube in order to count the gamma activity of cerium-144. Measurements of the gamma activity were carried out by a well-type NaI(Tl) scintillation countor, after a period of time, for the radioactive equilibria of cerium-144 and praseodymium-144.

Symbols and Formulae.—The following symbols and formulae are used:

$[\ ]$ = concentration in the aqueous phase

$[\ ]_o$ = concentration in the organic phase

HA = acetylacetone

D_A = distribution ratio of acetylacetone

$$D_A=[HA]_o/\{[HA]+[A^-]+[H_2A^+]\} \quad (1)$$

$D_A{}^o$ = distribution coefficient of acetylacetone

$$D_A^o=[HA]_o/[HA] \quad (2)$$

K_a = acid dissociation constant of acetylacetone

$$K_a=[H^+][A^-]/[HA] \quad (3)$$

K_b = base dissociation constant of acetylacetone

$$K_b=[H_2A^+]/[H^+][HA] \quad (4)$$

D_c = distribution ratio of cerium

D_c^o = distribution coefficient of ceric acetylacetone

$$D_c^o=[CeA_4]_o/[CeA_4] \quad (5)$$

K_n = formation constant of the chelate CeA_n

$$K_n=[CeA_n{}^{4-n}]/[Ce^{4+}][A^-]^n \quad (6)$$

k_m = formation constantant of the compounds $CeA_4\cdot m$HA in the organic phase

$$K_m=[CeA_4\cdot mHA]_o/[CeA_4]_o[HA]_o{}^m \quad (7)$$

Results and Discussion

The Distribution of Acetylacetone. — The equilibrium distribution ratio of acetylacetone varies with the pH of the aqueous phase. The variation depends on the dissociation of acetylacetone as an acid or a base. When it is assumed that ions are not extracted, the distribution ratio will be given as Eq. 1 or:

$$D_A=D_A^o/\{1+K_a/[H^+]+K_b[H^+]\} \quad (8)$$

Equation 8 indicates that D_A has a maximum value equal to $D_A^o/(1+2\sqrt{K_a\cdot K_b})$ at $pH=(pK_a-pK_b)/2$.

Since the prodct $K_a\cdot K_b$ is much smaller than unity, the maximum distribution ratio is reduced to D_A^o. A plot of D_A vs. pH at 25°C is given in Fig. 1. The distribution ratio is found to be almost constant in the pH range from 1.5 to 7, and D_A^o is determined graphically by Fig. 1. The distribution coefficients at various temperatures were determined in the same way; the results are summarized in Table I.

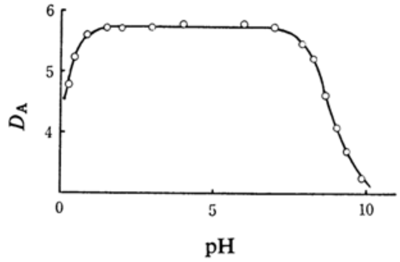

Fig. 1. Distribution curve of acetylacetone.

TABLE I. EQUILIBRIUM CONSTANTS OF ACETYLACETONE AT VARIOUS TEMPERATURES

Temp., °C	D_A^o	pK_a
10	5.5	8.9_0
25	5.4	8.8_8
40	5.3	8.8_6

When the term of $K_b[H^+]$ is small enough to be negligible compared with $K_a/[H^+]$, Eq. 8 is rewritten as:

$$D_A=D_A^o/\{1+K_a/[H^+]\},$$

or

$$\log\{(D_A^o-D_A)/D_A\}=pH-pK_a$$

A plot of $\log\{(D_A^o-D_A)/D_A\}$ as ordinate against pH as abscissa is given in Fig. 2. The pH value where D_A is equal to $D_A^o/2$ will be the pK_a of acetylacetone. The dissociation constants at various temperatures were obtained in the same way and are summarized in Table I; they are in good agreement with the literature.[3,4] The decrease in the distribution ratio is observed in the pH range below 1. Acetylacetone is assumed to be present in an acid form such as H_2A^+ in strong acid solutions.[4] The decrease in the distribution ratio may be attributed partially to the fact that the ionic strength in the pH range below 1 was not maintained constant, but mainly to the gradual transformation of acetylacetone into an acid form or a cationic form with a decreasing pH, which is incapable of being extracted with benzene.

The Distribution of Cerium.—The distribution ratio of cerium increases with an increase in the concentration of acetylacetone in the

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3) J. Rydberg, *Svensk Kem. Tid.*, **65**, 37 (1953).

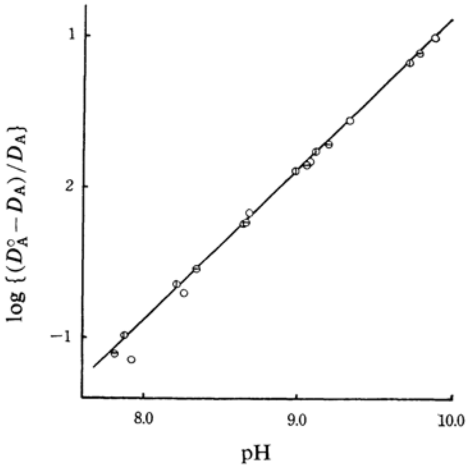

Fig. 2. Determination of pK_a of acetylacetone.
⊖ 10°C ○ 25°C ⦶ 40°C

organic phase, as is shown in Fig. 9, which suggests the presence of such compounds as $\mathrm{CeA}_N\cdot m\mathrm{HA}$ $(m, N \geqq 0)$ in the organic phase. Accordingly, the distribution ratio of cerium may be given as:

$$D_c = \sum_{m=0} [\mathrm{CeA}_N\cdot m\mathrm{HA}]_o / \sum_{n=0} [\mathrm{CeA}_n^{N-n}] \qquad (11)$$

where N is the number of the acetylacetonate ligand coordinated to cerium. In Eq. 11 it is assumed that the ionic species are not extracted in the organic phase.

The distribution curves of cerium are given in Figs. 3, 4, and 5 at 10, 25, and 40°C respectively. Fortunately, the distribution ratio of acetylacetone was proved to be constant under these experimental conditions, and the concentration of acetylacetone can easily be maintained constant, while changing that of the acetylacetonate ion in the aqueous phase, by changing the pH. In either Figs. 3, 4, or 5, straight lines with fourth-power dependence of the concentration of a hydrogen ion are obtained in the lower pH region. With an increase in the pH, however, the experimental values show a discrepancy from the straight lines downwards. If the tendency were due to the hydrolysis of cerium, the discrepancy would disappear when the concentration of acetylacetone in the system was increased against the experimental results. In Figs. 6, 7, and 8 the distribution of cerium is plotted against pA, $-\log[\mathrm{A}^-]$. Straight lines with fourth-power dependence of the concentration of the acetylacetonate ion in the higher pA region are also given. The distribution curves are observed to give the same slopes at the same pA value. The distribution ratio, however, increases with an increase in the concentration of acetylacetone in the organic phase. These results are adequately explained by Eq. 11, where N is substituted for 4, or Eq. 12;

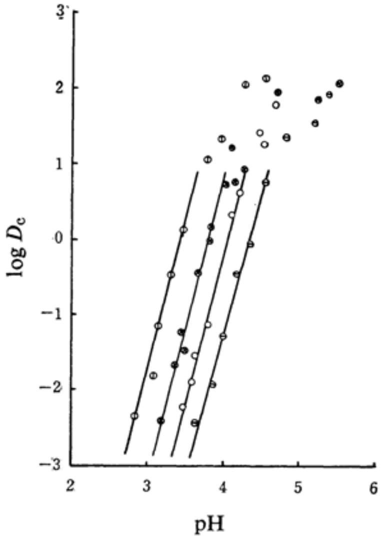

Fig. 3. Disrtibution curves of cerium as a function of pH at 25°C.
$[\mathrm{HA}]_o$, M: ⦶ 0.866, ⊗ 0.438, ○ 0.302, ⊖ 0.199

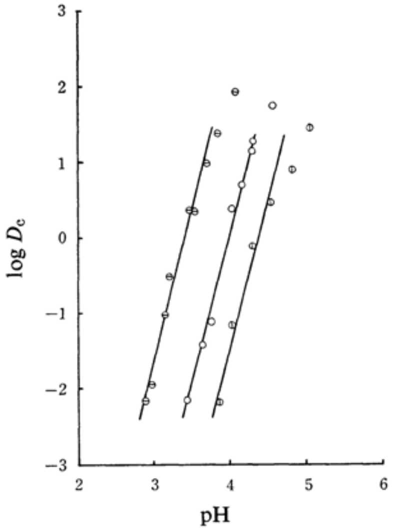

Fig. 4. Distribution curves of cerium as a function of pH at 10°C.
$[\mathrm{HA}]_o$, M: ⊖ 0.897, ○ 0.310, ⦶ 0.167

$$D_c = \sum_{m=0} [\mathrm{CeA}_4\cdot m\mathrm{HA}]_o / \sum_{n=0} [\mathrm{CeA}_n^{4-n}] \qquad (12)$$

Equation 12 is also supported by the early experimental results;[1] cerium(III) is not extracted, while in the presence of bromate cerium is extracted. By combining Eqs. 5, 6,

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[4] N. P. Rudenko and I. Stray, *Chem. Abstr.*, 53, 3971 (1959).

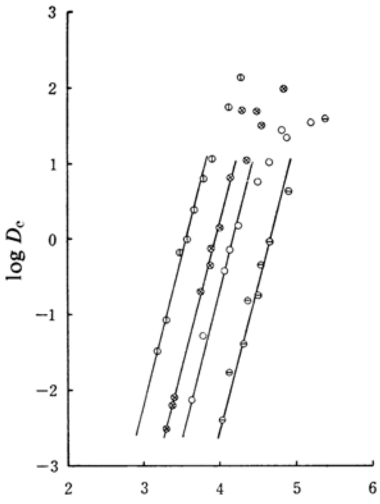

Fig. 5. Distribution curves of cerium as a function of pH at 40°C.
$[\mathrm{HA}]_o$, M: ⦶ 0.904, ⊗ 0.437, ○ 0.302
⊖ 0.155

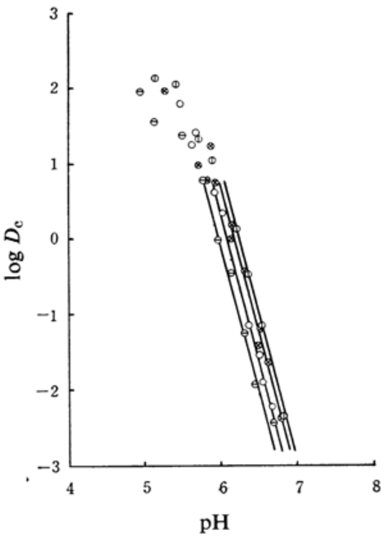

Fig. 5. Distribution curves of cerium as a function of pH at 25°C.
$[\mathrm{HA}]_0$, M: ⦶ 0.866, ⊗ 0.438, ○ 0.302
⊖ 0.199

7, and 12, D_c may be rewritten as:

$$D_c = D_c^\circ K_4 [\mathrm{A}^-]^4 \{ \sum_{m=0} k_m [\mathrm{HA}]_o^m \sum_{n=0} K_n [\mathrm{A}^-]^n \} \tag{13}$$

When the pA is high enough to make the products $K_n[\mathrm{A}^-]$ $(n \geqq 1)$ negligible compared with unity in the denominator in Eq. 13, that equation is reduced to:

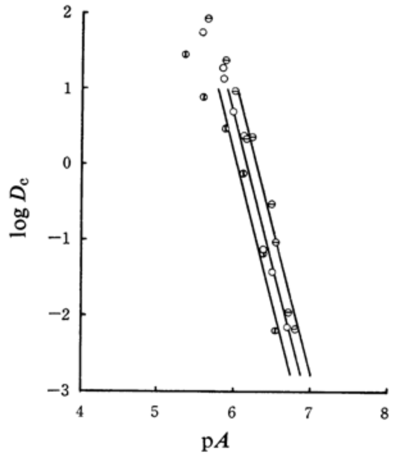

Fig. 7. Distribution curves of cerium as a function of pA at 10°C.
$[\mathrm{HA}]_o$, M: ⊖ 0.897, ○ 0.310, ⦶ 0.167

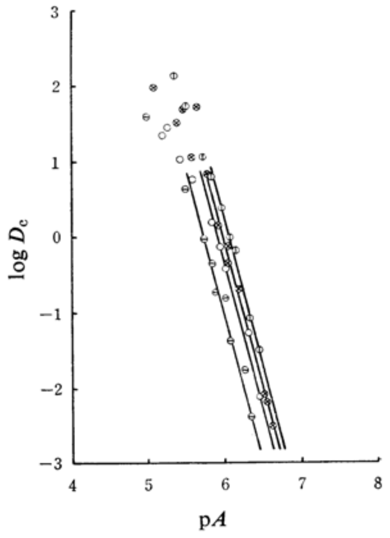

Fig. 8. Distribution curves of cerium as a function of pA at 40°C.
$[\mathrm{HA}]_o$, M: ⦶ 0.904, ⊗ 0.437, ○ 0.302
⊖ 0.155

$$D_c = D_c^\circ K_4 [\mathrm{A}^-]^4 \sum_{m=0} k_m [\mathrm{HA}]_o^m \tag{14}$$

Equation 14 indicates that in the higher pA region the distribution ratio of cerium is proportional to the fourth power of the concentration of the acetylacetonate ion for a constant concentration of acetylacetone in the organic phase. The reason why the distribution ratio is observed to bend gradually downwards may be explained by Eq. 13 to be the result of the gradual formation of ceric acetylacetonate, CeA_n^{4-n} $(n \geqq 1)$, in the aqueous phase, because distribution curves at the respective concentrations of acetylacetone seem to give the same slope at the same p*A* values in Figs. 6, 7, and 8. The distribution data, however, were considerably scattered, and the reproducibility was somewhat poor in the higher pH region, where gradual hydrolysis may take place. Therefore, the stoichiometric treatments were not applied in the lower p*A* regions.

The variations in the distribution ratio with the concentration of acetylacetone in the organic phase are given in Fig. 9, which was obtained by interpolating the distribution curves of Figs. 6, 7, and 8 at p*A* 6.25. The increase in the distribution ratio of cerium with an increase in the concentration of acetylacetone in the organic phase is comprehensible as the results of the formation of the compounds, $CeA_4 \cdot mHA$ in the organic phase, which is explained by Eq. 14 (Fig. 9). Since the distribution ratio is proportional to the square of the concentration of acetylacetone below 0.5 M, it may be concluded that a molecule of cerium acetylacetonate combines with two molecules of acetylacetone to form a compound $CeA_4 \cdot 2HA$ in the organic phase.

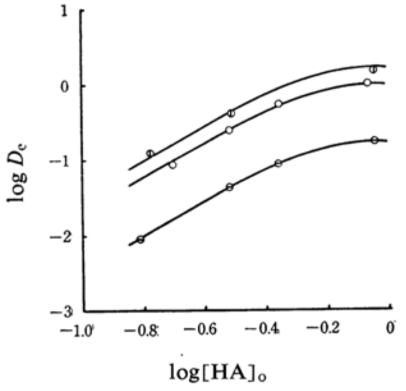

Fig. 9. Distribution curves of cerium as a function of $[HA]_o$ at p*A* 6.25.
Temp., °C: ⦶ 10, ○ 25, ⊖ 40

The effects of the temperature on the distribution ratio of cerium are given in Fig. 9. The effects of the temperature are small for reactions 1, 2, and 3. Supposing that reactions 5 and 6 are not so much influenced by the temperature as usual, reaction 7 has to be influenced by the temperature. The enthalpy change of reaction 7 was calculated to be −13 kcal. from Fig. 9 on the above assumption ($\Delta \log D_c = 1$ for $\Delta T = -30°$). If the interaction between benzene and CeA_4 does not amount to any appreciable amount, the enthalpy change is regarded as the binding energy between CeA_4 and 2HA. The magnitude of the energy needed for a molecule of acetylacetone to bind with CeA_4 is 6.5 kcal., which corresponds to the energy of hydrogen bond. The discrepancy from the straight line in the higher concentration regions is assumed to be the result of the saturation of hydrogen bonds for CeA_4 to combine with molecules of acetylacetone, or to be the result of changes in the solvent properties of benzene resulting from an increase in the concentration of acetylacetone in the organic phase.

Summary

The extraction behavior of tracer amounts of cerium-144 with acetylacetone has been studied. The distribution ratio of acetylacetone between benzene and a 0.1 M sodium perchlorate solution is constant in the pH range 1.5−7, and the distribution coefficients have been determined to be 5.5, 5.4, and 5.3 at 10, 25, and 40°C respectively. The distribution ratio of cerium has been shown to be proportional to the fourth power of the concentration of the acetylacetonate ions and to the square of that of acetylacetone in the organic phase. From these results, it has been concluded that cerium exists as a tetravalent ion in the system and that the chemical form of cerium extracted in the organic phase is $CeA_4 \cdot 2HA$. Two molecules of acetylacetone are assumed to combine with CeA_4 forming hydrogen bonds.

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