Studies on Solvent Extraction using Radioactive Isotopes. VIII[1]. *Solvent Extraction of Cerium with Acetylacetone*

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The separation of cerium by solvent extraction with ethyl ether or methyl isobutyl ketone from a nitric acid medium has been studied by Imre[1] and by others[3-5], but their methods are tedious in order to avoid the hazard of an explosion of the solvent by concentrated nitric acid. Recently, however, an extraction with di(2-ethylhexyl) orthophosphoric acid and thenoyltrifluoroacetone has been reported[6,7].

It has been known that acetylacetone forms with cerium a chelate compound such as $Ce(C_5H_7O_2)_4$ which dissolves in organic solvents[8,9]. There is no report, however, on the extraction behavior of cerium with acetylacetone. The authors have therefore investigated the various conditions such as acetylacetonate, having an effect on the extraction of cerium.

Experimental

Reagents.—Acetylacetone on the market usually contains considerable amounts of acetic acid; therefore, it was purified as follows: One liter of acetylacetone was washed with 100 ml. of ammonia water (1 : 10), then washed twice with 100 ml. portions of water, and distilled. The distillation fraction of 138°C was collected and used. Carrier-free cerium-144 ($^{144}CeCl_3$) used as a tracer was imported from England; a part of this was diluted to 1 M nitric acid with an activity of about 10^6 c. p. m./ml.

Cerium stock solutions (10^{-2} M) of cerium(III) and cerium(IV) were prepared by dissolving the guaranteed-grade reagents of cerous nitrate and ceric sulfate in 1 M nitric acid respectively; the concentrations of the stock solutions were determined by titration with ferrous sulfate potentiometrically. More dilute solutions were prepared fresh before use from the stock solutions.

Sodium bromate, sodium acetate and other reagents were all guaranteed-grade reagents.

Redistilled water was used.

Apparatus.—For measurements of radioactivity, a well-type scintillation counter, Model RSP-1, made by Kobe Kogyo Co., Japan, was employed. For measurements of the pH of the aqueous phase, a glass electrode pH meter, Model GU-1, made by Shimadzu Co., Japan, was used.

General Procedure.—The general procedure is, unless otherwise stated, as follows: To a stoppered Erlynmeyer flask containing cerium (5×10^{-6} M) and ^{144}Ce, add sodium bromate, acetylacetone, and acetate buffer (20 ml.), and make up the volume to a constant (40 ml.) with water. Mix well for two minutes and let it stand. Every suitable period take out an aliquot (5 ml.) into a separatory funnel and extract the cerium acetylacetonate with 2 ml. of benzene by shaking for one minute. After the phases have separated, transfer the organic and the aqueous phases into two test tubes and let them stand for more than four hours till the radioactive equilibrium of ^{144}Ce and ^{144}Pr has been established; then measure the radioactivity of both phases and the pH of the aqueous phase.

Results and Discussion

Concentration of Acetylacetone.—As will be shown in the later part of this paper, cerous cerium is not extracted with acetylacetone by shaking for 40 min. Accordingly, it is necessary to oxidize cerium to the ceric state. The

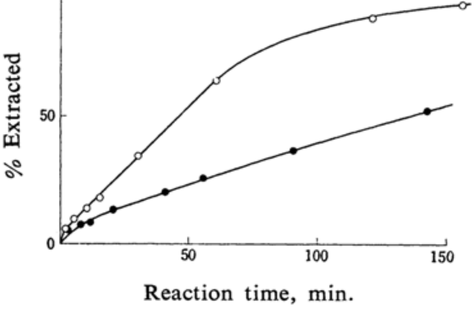

Fig. 1. Effect of concentration of HA.

(HA: Acetylacetone)
○: [HA] 1.2 M
●: [HA] 0.61 M
[$NaBrO_3$] 0.15 M

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[1] Paper VII of this series: N. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 437 (1960).
[2] L. Imre, *Z. anorg. u. allgem. Chem.*, **151**, 214 (1927).
[3] A. W. Wylie, *J. Chem. Soc.*, **1951**, 1417.
[4] E. C. Pitzer, U. S. Pat. 2615798 (Oct. 28, 1952).
[5] L. E. Glendenin, K. F. Flynn, R. F. Buchanan and E. P. Steinberg, *Anal. Chem.*, **27**, 59 (1955).
[6] D. F. Peppard, G. W. Mason and S. W. Moline, *J. Inorg. Nucl. Chem.*, **5**, 141 (1957).
[7] G. W. Smith and F. L. Moore, *Anal. Chem.*, **29**, 448 (1957).
[8] Beilsteins Handbuch der Organischen Chemie, 4. Aufl., Bd. 1, p. 402, Julius Springer, Berlin.
[9] W. C. Fernelius, "Inorganic Synthesis", Vol. II, McGraw-Hill Book Co., Inc., New York (1946), p. 13.

authors used sodium bromate as an oxidizing agent.

The relation between the amounts of the chelate extracted and the reaction time is shown in Fig. 1. The reaction rate of cerium with acetylacetone is quite slow at room temperature. Even though the large excess of acetylacetone, such as 0.6 M acetylacetone, is used, complete extraction is not obtained.

Concentration of Bromate.—The concentration of bromate has a great influence on the oxidation of cerium, viz., on the extraction from cerous state, as is shown in Fig. 2. It is conceivable from the results in Figs. 1 and 2 that the rate of increase in the extraction percentage against the time elapsed is approximately proportional to the concentration of acetylacetone and bromate, but the discrepancy from the linear proportionality in the case of bromate of a higher concentration can be presumed to be due to the formation of complexes of ceric ion with bromate ion or bromide ion.

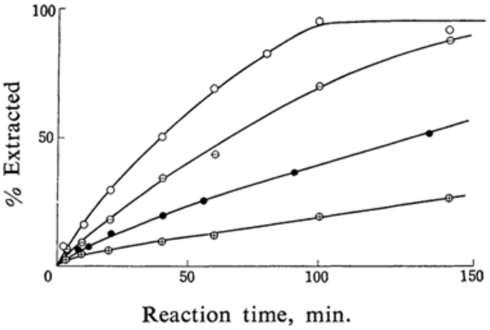

Fig. 2. Effect of concentration of NaBrO$_3$.

[NaBrO$_3$] ○: 0.65 M
⊖: 0.33 M
●: 0.16 M
⊕: 0.065 M
[HA] : 0.61 M

Direct Extraction with Acetylacetone in Benzene.—A comparison was made between the following two cases:

(1) Acetylacetone was added to the aqueous solution and left to standing for 2.5 hr. Every suitable period, the chelate was extracted with benzene as described in the general procedure.

(2) Acetylacetone was added as benzene solution, and direct extraction of the chelate was carried out by shaking for a suitable period.

The amounts of acetylacetone used in the two cases were equal. As is shown in Fig. 3, the results of the two cases are, however, considerably different; the results in the latter case are lower. This may be expected from Fig. 1; i. e., the concentration of the acetylacetone distributed in the aqueous phase is decreased by the presence of benzene.

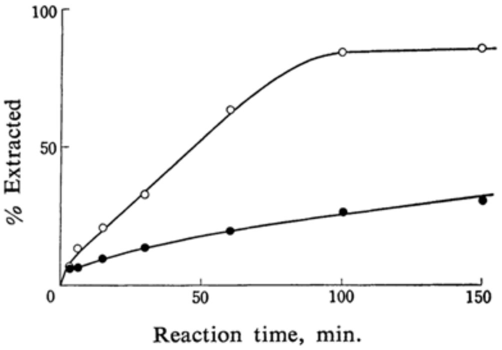

Fig. 3. Comparison of two types of extraction.

○: Extraction by benzene after acetylacetone was added to aqueous solution

●: Direct extraction with acetylacetone in benzene

Oxidation State.—In order to confirm the effects of the oxidation state and the oxidation process, the authors carried out some experiments on various combinations of carrier cerium and ^{144}Ce.

(1) Cerium(III) and ^{144}Ce with 0.61 M acetylacetone.

(2) Cerium(IV) and ^{144}Ce with 0.61 M acetylacetone.

(3) Cerium(IV) and ^{144}Ce with 0.61 M acetylacetone, but in this case ^{144}Ce was pretreated by being left standing overnight in a solution of 0.17 M bromate at pH 2.2.

(4) Cerium(IV) and ^{144}Ce with 0.61 M acetylacetone, but in this case ^{144}Ce was pretreated by being left standing overnight in a solution of 0.17 M bromate and 1 M nitric acid.

(5) Cerium(IV) and ^{144}Ce the same as Exp. 3, except that the concentration of acetylacetone was 1.2 M.

In all cases the concentration of cerium(III) and cerium(IV) was 1.0×10^{-6} M. The results are presented in Fig. 4. It can be observed that cerium in a cerous state can not be extracted with acetylacetone without an oxidizing agent. When cerium(IV) and pretreated ^{144}Ce are used, 50% extraction is obtained as a maximum. This is probably owing to the hydrolysis of cerium(IV). Therefore, though ceric cerium is extracted with acetylacetone, it is not desirable to oxidize cerium before the addition of acetylacetone.

The result of Exp. 2 shows that the exchange reaction is fairly slow. Consequently, in spite of the long reaction time, the apparent extraction remains low.

When an aqueous solution containing carrier-free ^{144}Ce is shaken with acetylacetone in benzene, ^{144}Ce is rapidly extracted[10]. On the basis of the results in Exp. 1, cerous cerium in ordinary concentration can not be extracted.

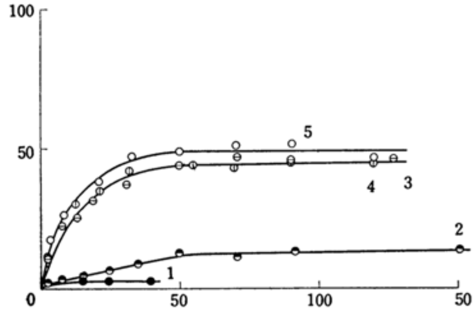

Fig. 4. Effect of oxidation states of carrier and tracer cerium. [HA] ; 0.61 M

	Oxidation state Carrier	 Tracer
(1)	III	III
(2)	IV	III
(3), (4), (5)*	IV	IV

* [HA] ; 1.2 M

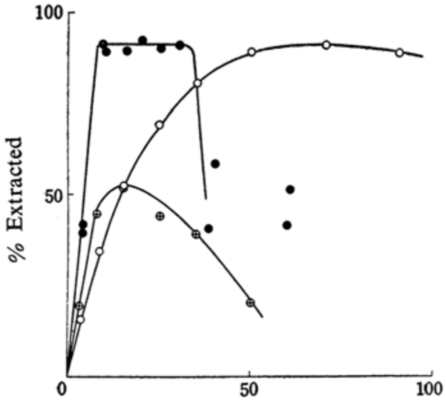

Fig. 5. Effect of concentration of reagents at 40°C.

	[HA], M	[NaBrO$_3$], M
●	0.61	0.33
⊕	0.61	0.065
○	0.15	0.33

This is one of the most characteristic features of the carrier-free ^{144}Ce. The details of this problem are now being examined.

Effect of Heating. — As described in the previous part, a fairly long time is necessary for complete extraction, but the reaction is accelerated by heating. After cooling to room temperature, the extraction with benzene was carried out. The effect of the concentration of reagents at 40°C is shown in Fig. 5.

The results with various concentrations of cerium at 40°C are shown in Fig. 6. Though heating is effective, the yield is low at about 5×10^{-5} M cerium. In every case in Figs. 5 and 6, the effect of heating is accompanied by the simultaneous disadvantage of the destruction of the chelate compound by hydrolysis. Care should be taken not to heat too long. Ten minutes heating is the best. At room temperature, however, the chelate is found to be fairly stable in the organic phase.

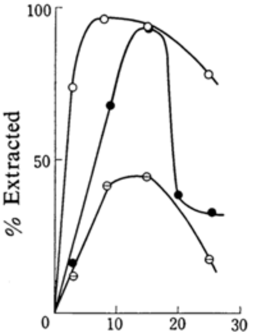

Fig. 6. Extraction of various concentration of cerium carrier (at 40°C).

[HA] ; 0.98 M, [NaBrO$_3$] ; 0.40 M

[Ce^{3+}] ○: 5×10^{-6} M
●: 2.5×10^{-5} M
⊖: 5×10^{-5} M

The authors arranged the standard procedure for extraction as follows: A mixture containing 1 ml. of cerium(III)[11], 1 ml. of 2 M sodium bromate, 0.5 ml. of acetylacetone, and 2.5 ml. of the acetate buffer solution is heated at 40°C for the minutes. After cooling to room temperature, the chelate is extracted with 2 ml. of benzene by shaking for one minute.

Extraction and Back-extraction. — The extraction curve of cerium by the standard procedure is shown in Fig. 7. In comparison with the extraction curve of carrier-free ^{144}Ce[10], the optimum pH range is quite narrow, but it is not difficult to adjust the pH of the aqueous phase to about 5~6 with an acetate buffer solution.

In order to investigate the distribution of cerium between benzene and the aqueous phase, and in order to find the suitable conditions for the back-extraction of cerium, an aliquot (2 ml.) of the benzene solution containing chelate prepared by the standard procedure was shaken for 1 min.[12] with each 5 ml.

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[10] This is shown in Part IX of this series, This Bulletin, 35, 237 (1961).

[11] In the final aqueous solution the concentration of Ce(III) is 5×10^{-6} M.

[12] One minute was found to be enough for the extraction.

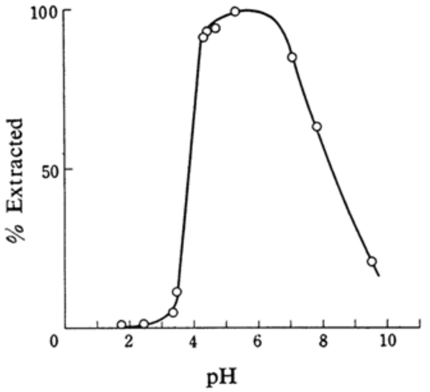

Fig. 7. Extraction curve of cerium. [HA] ; 0.81 M, [$NaBrO_3$] ; 0.33 M

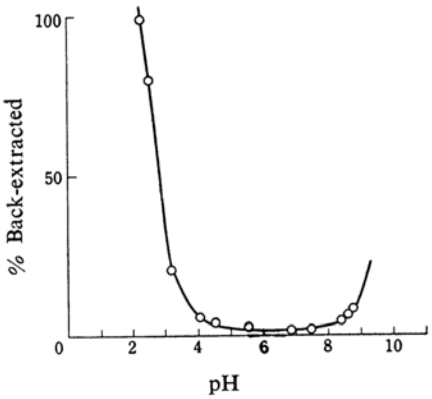

Fig. 8. Back-extraction of cerium from organic phase.

of the buffer solution or with dilute nitric acid.

As shown in Fig. 8, cerium extracted in benzene is easily stripped with a dilute acid, e. g., 0.1 M nitric acid. The chelate in the organic phase is not appreciably influenced by washing with the buffer solution of pH 4∼8. The pH range is considerably wider than that of the extraction (cf. Fig. 7), but it is almost the same as the extraction curve of carrier-free ^{144}Ce[10]. Consequently, it is proper to consider that cerium was hydrolyzed in the region of pH 7∼8.

Coexisting Substances. — Table I shows the effects of inorganic salts and organic acids. Of the substances tried phosphate, oxalic acid, citric acid, tartaric acid, and EDTA (disodium salt) cause severe interference, even with such a low concentration as ca. 10^{-2} M. A little interference is observed with nitrate and sulfate. Chloride shows a more complicated interference. This is perhaps owing to the reduction effect of chloride ion in the case of cerium.

TABLE I. EFFECTS OF COEXISTING SUBSTANCES

Salt or acid	Concn., M	Acetylacetonate % extracted
$NaNO_3$	0.03	97.4
	0.08	94.4
	0.2	91.6
Na_2SO_4	0.03	92.1
	0.07	90.7
NaCl	0.03	71.0
	0.08	48.5
KH_2PO_4	0.03	9.2
	0.08	4.2
Oxalic acid	0.007	3.6
	0.02	0.6
Citric acid	0.007	4.9
	0.02	1.2
Tartaric acid	0.03	7.6
EDTA	4×10^{-4}	1.0

Summary

The extraction of cerium with acetylacetone was studied, using ^{144}Ce as a tracer. Cerous cerium can not be extracted without an oxidizing agent. After the mixture of 0.61 M acetylacetone, 0.65 M sodium bromate and 5×10^{-6} M cerium had been left standing for 100 min. at pH 5∼6, 95% of the cerium was extracted in benzene. The reaction was accelerated by heating, e. g., at 40°C, or by increasing the concentration of acetylacetone and bromate. Care should be taken not to heat too long, thus avoiding the decomposition of the chelate by hydrolysis. The presence of phosphate, oxalic acid, citric acid, tartaric acid and EDTA caused severe interference.

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