Conf-680913--1

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EXTRACTION STUDIES OF CERIUM(III) INTO DI-(2-ETHYLHEXYL)PHOSPHORIC ACID AND
THE OBSERVATION OF ITS OXIDATION IN THE PRESENCE OF CONCENTRATED NITRATE
SOLUTIONS TO FORM A Ce(IV) - NITRATE - DEHP COMPLEX*

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September, 1968

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*Prepared for presentation at the 5th International Conference on Solvent Extraction Chemistry, Jerusalem, Israel, Sept. 16-18, 1968.

**This paper is based on work performed under United States Atomic Energy Contract AT(45-1)-1830.

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EXTRACTION STUDIES OF CERIUM(III) INTO DI-(2-ETHYLHEXYL)PHOSPHORIC ACID AND
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Many techniques for the separation of cerium from the other rare earths have been reported, almost all based on the oxidation of cerium to the tetravalent state, followed by its preferential extraction. Silver-catalyzed persulfate¹ and electrolysis² with HDEHP, electrolysis³ and ozone⁴ with TBP, and 10M HNO_3 - KBrO_3 ⁵ with dioctylphosphoric acid are such examples. Recently we noted that a yellow Ce(IV) complex was obtained when Ce(III) was extracted by HDEHP and then washed with high nitrate concentrations (6-7M) of various inorganic salt solutions [Na(I), Sr(II), Ce(III), or Al(III)], or when Ce(III) was extracted directly from these concentrated nitrate solutions. When Ce(III) was extracted into HDEHP from very dilute nitrate solutions or from solutions containing other anions such as Cl^- , $\text{SO}_4^{=}$, or OH^- , the organic phase remained colorless. Since the oxidation potential of the Ce(III)-Ce(IV) couple is -1.61 volts, this observation of cerium oxidation in the presence of high nitrate solutions and HDEHP appeared worthy of further study.

This paper discusses the solvent extraction of cerium with HDEHP and the formation of Ce(IV) as a function of nitrate, HDEHP, metal cation, and hydrogen ion concentration. Peppard and Ferraro⁶ had previously determined that the extraction of Ce(IV) into a HDEHP-toluene phase from a saturated $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$

solution gave a yellow organic phase with a complex represented as

$\left[\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2 \right]_n$. We have prepared the Ce-DEHP compound resulting from the extraction of Ce(III) from high nitrate solutions and have compared this compound with that of Peppard and Ferraro through elemental analysis, I. R. spectrometry, and vapor pressure osmometry.

EXPERIMENTAL

The HDEHP purified by the method of Partridge and Jensen⁷ was colorless, free of H₂MEHP, and had an experimental equivalent weight of 322.7 ± 0.5 . The organic diluent used for the solvent extraction studies was a highly refined mixture of normal paraffin hydrocarbons, C₁₀ to C₁₄, manufactured by the South Hampton Co., Houston, Texas. All other chemicals were reagent grade and were used as purchased except where noted.

The distribution coefficients were determined by stirring the two equal volume phases at $25.0 \pm 0.5^\circ\text{C}$ in a constant temperature bath, separating the two phases by centrifugation, and analyzing the cerium or promethium radioisotopes by their gamma or bremsstrahlung energies. Since we have observed that the cerium distribution coefficient is time dependent, a 10 minute contact time was selected for use in this study unless otherwise noted. Gamma-ray counting was performed by a RIDL 400-channel analyzer, Model 24-2, which has a thallium-activated NaI 3 inch crystal detector. CePr-144 and Pm-147 radiotracers were prepared by ion exchange purification.

The organic required for the D_{strip} values, fig. 1, was obtained by extracting cerium into 0.25M HDEHP from a 0.01M HNO₃ solution containing 0.01M Ce(NO₃)₃ or (NH₄)₂Ce(NO₃)₆. The Ce(IV) organic was then washed with 2M HNO₃ to remove possible traces of Ce(III) prior to determining the Ce(IV) D_{strip} data. The Pm-147 radiotracer was extracted with 0.01M Ce(III) into HDEHP.

The I. R. spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. The molecular weight determinations were obtained using a Mechrolab Model 302 vapor pressure osmometer.

RESULTS AND DISCUSSION

Solvent Extraction Studies

To more fully understand the mechanism of cerium oxidation and extraction, we first determined the stripping or back extraction distribution coefficients, D_{strip} , for Ce(III), Ce(IV), and Pm(III) as a function of the nitric acid concentration, fig. 1. Promethium values were determined to represent the non-oxidizable trivalent rare earths. The large separation factor, $\underline{S}_{\text{Pm(III)}}^{\text{Ce(IV)}}$, at hydrogen ion concentrations of 0.5 to 5M, is the basis for cerium - rare earth separation. The D_{strip} values for Ce(III), Pm(III), and Ce(IV) with 2M HNO₃ were 0.001, 0.005, and 10, respectively. Therefore, as we investigated other variables such as HDEHP, hydrogen ion, nitrate, and metal cation concentrations, the D_{strip} provided a measure of cerium oxidation.

Extraction $\underline{D}_{\text{Ce}}$ values were determined for 2M Al(NO₃)₃, 0.01M Ce(III) as a function of the HDEHP concentration, fig. 2. No attempt was made to control the equilibrated aqueous hydrogen ion concentration which varied from 0.050M to 0.113M for 0.1M to 2M HDEHP. The results show that when the organic phase was subsequently stripped with 2M HNO₃ that the $\underline{S}_{\text{Pm}}^{\text{Ce}}$ varied from 1000 to 50 with 0.1M to 2M HDEHP. If Ce(III) had not oxidized, we should expect the $\underline{S}$ to be 3 at 0.25M HDEHP, fig. 1. If the cerium in the organic phase were completely oxidized we should expect $\underline{S}$ to be greater than 3000. The results, fig. 2, indicate that a partial oxidation does occur when Ce(III) is extracted from 2M Al(NO₃)₃ into HDEHP with a 10 minute contact, since the actual $\underline{S}$ value for 0.25M HDEHP was 570.

Extraction D_{Ce} values were obtained as a function of total nitrate for NaNO_3 and $\text{Al}(\text{NO}_3)_3$. The organic phase was subsequently stripped with 2M HNO_3 to determine the effect of nitrate and metal cation on the amount of $\text{Ce}(\text{III})$ oxidized. The results, shown in table 1, have been converted to percent of the original cerium concentration. The values show that as the nitrate concentration decreases, the percent of the cerium extracted into the organic phase increases, the percent of the cerium remaining in the organic (after stripping with 2M HNO_3) decreases, and thus the ratio $[\text{Ce}]_{\text{org strip}}/[\text{Ce}]_{\text{org ex}}$ decreases. The results also show that the oxidation of $\text{Ce}(\text{III})$ with equal nitrate concentrations is enhanced for $\text{Al}(\text{III})$ as compared to $\text{Na}(\text{I})$, if we assume that the cerium remaining in the organic phase after stripping is $\text{Ce}(\text{IV})$. For 2M $\text{Al}(\text{NO}_3)_3$ and 6M NaNO_3 the percent of the initial cerium found as $\text{Ce}(\text{IV})$ in the stripped organic (table 1) is 24.3 and 4.2, respectively, which is 91 percent of that oxidized during the initial extraction (based on the $D_{\text{Ce}(\text{IV}) \text{ strip}}$ value of 10, fig. 1).

Values for D_{Ce} were determined for 0.25M HDEHP as a function of the equilibrated aqueous hydrogen ion concentration (as determined by titration of the aqueous phase after extraction) for $\text{Al}(\text{III})$, $\text{Sr}(\text{II})$, and $\text{Na}(\text{I})$ salt solutions containing 6M NO_3^- . $D_{\text{Ce strip}}$ values were obtained for 2M HNO_3 . The results, shown in table 2, have been converted to percent of the original cerium concentration and show that the oxidation of $\text{Ce}(\text{III})$ is enhanced by low hydrogen ion concentrations. The results also show that at low hydrogen ion concentrations, the percent of the total cerium remaining as $\text{Ce}(\text{IV})$ in the stripped organic phase decreases in the order $\text{Al}(\text{III}) > \text{Sr}(\text{II}) > \text{Na}(\text{I})$.

The results in table 2 with 2M $\text{Al}(\text{NO}_3)_3$, 0.01M $\text{Ce}(\text{III})$, and 0.06M H^+ indicate that 53 percent of the initial cerium extracted into 0.25M HDEHP,

Table 1

Cerium Concentration in the Organic Phase
as a Function of the Nitrate Concentration

Organic: 0.25M HDEHP

Aqueous Extraction: 0.01M Ce(III) + Al(III) or Na(I) nitrate

Aqueous Strip: 2M HNO₃

	<u>NO₃⁻, M</u>	<u>H⁺, M</u>	<u>Percent of 0.01M Cerium in the Organic</u>		<u>Percent of the</u>
			<u>After Extraction</u>	<u>After Stripping</u>	<u>Extracted Cerium</u> <u>in the Stripped Organic</u>
Al(III)	6	0.060	52.5	24.3	46.3
	3	0.054	55.0	4.1	7.5
	1.5	0.059	70.3	4.6	6.5
	0.75	0.059	80.1	0.16	0.2
	0.06	0.059	91.0	0.09	0.1
Na(I)	8	0.023	79.3	9.4	11.9
	6	0.026	83.8	4.2	5.0
	3	0.029	92.7	1.0	1.1
	0.6	0.030	98.2	0.1	0.1

Table 2

Cerium Concentration in the Organic Phase
as a Function of the Hydrogen Ion Concentration

Organic: 0.25M HDEHP

Aqueous Extraction: 0.01M Ce(III) + 6M NO₃⁻ as Al(III), Sr(II), or Na(I) + H⁺

Aqueous Strip: 2M HNO₃

	H ⁺ , M	Percent of 0.01M Cerium in the Organic After Extraction	Percent of the Extracted Cerium After Stripping	Percent of the Extracted Cerium in the Stripped Organic
2M Al(NO ₃) ₃	0.060	52.5	24.3	46.3
	0.097	37.1	17.6	50.1
	0.120	29.5	16.2	54.9
	0.223	11.0	7.0	63.6
	0.487	2.0	1.5	75.0
	1.06	0.64	0.016	2.5
3M Sr(NO ₃) ₂	0.038	82.	6.8	8.3
	0.070	42.5	8.5	20.0
	0.115	21.9	6.8	31.0
	0.200	7.4	3.8	51.3
	0.487	1.0	-	-
6M NaNO ₃	0.023	83.8	4.2	5.0
	0.076	39.0	7.0	17.9
	0.120	18.0	5.8	32.2
	0.216	5.7	3.0	52.6
	0.470	1.0	-	-

24 percent remained in the organic phase after stripping with $2M$ HNO_3 , or that 46 percent of the extracted cerium remained in the stripped organic phase. To determine if the percent oxidation was dependent on the initial cerium concentration, values for extraction and stripping were determined for initial $Ce(III)$ concentrations from 0.001 to $0.3M$. The value $[Ce]_{org\ strip}/[Ce]_{org\ ex} \cdot 100$ varied from 75 to 42 percent as shown in fig. 3. The values above $0.002M$ Ce varied 46 ± 4 percent. Thus, it was determined that in the concentration range from $0.002M$ to $0.3M$ $Ce(III)$, the percent of the extracted cerium oxidized during a 10 minute contact time is independent of the initial aqueous cerium concentration.

Oxidation of $Ce(III)$ in the Absence of Air

To determine if the $Ce(III)$ -(IV) reaction was an air oxidation reaction, a set of experiments was performed with an argon-sparged system. A saturated, colorless solution of $Ce(NO_3)_3$ and an equal volume of $0.3M$ HDEHP-toluene solution were each sparged with argon for 20 minutes prior to contact under an argon atmosphere. Upon contact and mixing of the two phases, the organic phase became visibly yellow within 30 seconds and was bright yellow within 2-3 minutes. Mixing continued for 15 minutes. The two phases were then separated, the aqueous phase was sparged with argon again and recontacted under an argon atmosphere with a second argon-sparged $0.3M$ HDEHP-toluene solution. Again, there was a definite yellow color in the organic phase after 30 seconds and was bright yellow within 2-3 minutes.

To check the effect of a nitrite ion suppressant on the rate of reaction, the above experiment was repeated with $0.25M$ sulfamic acid in the aqueous phase. There was no color development observed in the organic phase for 30 minutes. The experiment was repeated with $0.025M$ sulfamic acid and again there was no

visible color in the organic phase for 30 minutes, indicating that nitrite ion is required for the rapid oxidation of the Ce(III) in this system.

Preparation of Cerium-DEHP Salts

The Ce(III)-DEHP salt was prepared by contacting HDEHP - toluene with a saturated aqueous solution of $\text{Ce}_2(\text{SO}_4)_3$. The resulting clear organic phase was concentrated by partial evaporation of the toluene and the salt was then precipitated by the addition of acetone. The precipitate was filtered, washed with acetone and dried. A white wax-like solid was obtained.

The Ce(IV)-DEHP salt was prepared by contacting HDEHP - toluene with a saturated solution of $\text{Ce}(\text{NO}_3)_3$ for several hours. The loaded organic phase which became yellow in color in less than 1 minute after contact was subsequently treated as above for preparation of the solid compound. A yellow solid was obtained which was less wax-like than the Ce(III) compound above.

A Ce(IV)-DEHP salt was also prepared by the method of Peppard and Ferraro⁶ with the modification that instead of evaporating the toluene to complete dryness, the solid was precipitated by the addition of acetone after partial evaporation of the toluene.

The cerium-DEHP salts were dried in a vacuum oven at 50°C and stored in a dessicator.

Chemical Analysis of Ce-DEHP Salts

Chemical analysis of the Ce(III) salt showed it to be $\text{Ce}(\text{DEHP})_3$. The results, with the theoretical values in parentheses, were 52.0% C (52.2), 8.7% P (8.4), and 9.6% H (9.3). The results for the Ce(IV) salt obtained from the oxidation of Ce(III), compared with the theoretical values for

$\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$ in parentheses, were 47.6% C (45.1), 7.6% P (7.3), 8.7% H (8.0), and 1.64% N (1.64). The corresponding values for the Ce(IV) salt prepared by the method of Peppard and Ferraro were 46.7% C, 7.4% P, 8.6% H, and 1.69% N. The respective values for the two Ce(IV) salts are within experimental error of each other and thus show that the salts have the same chemical composition. The values clearly indicate that there is one N atom and two DEHP^- ions per Ce. Peppard and Ferraro postulated one hydroxyl or one-half oxygen per Ce in the compound to balance the charges; and since no O-H peaks were observed in the I. R. spectrum, they concluded that the formula was $[\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2]_n$. Our results agree with their conclusions concerning the formula and also show that the same compound is formed by the two methods.

I. R. Spectra of Cerium-DEHP Salts

Infrared spectra of the two Ce(IV)-DEHP salts in CCl_4 are shown in fig. 4. The spectrum of HDEHP and the Ce(III)-DEHP salt are included for comparison. The spectrum of the Ce(III) salt differs from that of the Ce(IV) salt, of course, by the absence of the NO_2 symmetric and antisymmetric stretching vibrations in the 7.8-7.9 and 6.5-6.7 micron regions, respectively. The P=O stretching band (at 8.15 μ for HDEHP) occurs at 8.55 μ for the Ce(III) compound and at 8.63 μ for the Ce(IV) compound. The spectra of the two Ce(IV)-DEHP salts are the same and agree with that reported by Peppard and Ferraro for $\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$.

Molecular Weight Determination of the Ce-DEHP Salts

Osmometric data for the Ce-DEHP salts at 37°C are shown in fig. 5. The lines drawn on the figures for the various degrees of polymerization are based on redistilled TBP in spectrograde cyclohexane as the standard for calibration

of the matched thermistors. Each data point shown for the cerium salts is the average of at least three Wheatstone bridge readings, ΔR , at a given concentration. The concentration values shown are the number of gram formula weights of the monomer per 1000 grams of cyclohexane. The Ce-DEHP salts were found to be highly polymerized in cyclohexane making it difficult to obtain vapor pressure data at higher concentrations because of the high viscosity of the solutions. These data indicate that the degree of polymerization for $\text{Ce}(\text{DEHP})_3$ in cyclohexane is 16 ± 1 and that for $\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$ the degree of polymerization is 18 ± 4 for the concentration range studied.

SUMMARY

Cerium(III) is oxidized to Ce(IV) in the presence of nitrate ion and HDEHP to form a mixed Ce(IV)-nitrate-DEHP complex in the organic phase. The reaction is influenced by the nitrate, metal cation, and hydrogen ion concentrations. The percent of the initial cerium which is oxidized during a 10 minute contact time increases as the nitrate ion concentration increases (up to $6\text{-}8\text{M}$) and as the hydrogen ion concentration decreases (down to 0.06M). While the initial cerium concentration has an effect on the amount of cerium extracted, the percent of the extracted cerium oxidized is independent of the initial cerium concentration.

A salting effect by other metal ions was observed when extracting cerium from Al(III), Sr(II), and Na(I) nitrate solutions. The amount of Ce(IV) formed decreases in the order $\text{Al(III)} > \text{Sr(II)} > \text{Na(I)}$ for solutions having equal nitrate and hydrogen ion concentrations.

Separation factor values, $S_{\text{Pm}}^{\text{Ce}}$, between 2M $\text{Al}(\text{NO}_3)_3$, 0.01M Ce(III) and 0.1M to 2M HDEHP were 1000 to 50, respectively.

The oxidation reaction is equally fast in an argon or an air atmosphere. The rate of reaction is greatly reduced by the presence of a nitrite ion suppressant, such as sulfamic acid, indicating that nitrite ion is necessary for rapid oxidation of the Ce(III) in this system.

The Ce(IV)-DEHP salt resulting from this oxidation of Ce(III) was prepared and compared through I. R. spectroscopy, elemental analysis, and vapor pressure osmometry to that obtained by extracting Ce(IV) from a saturated $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution. The two salts were found to be identical, having the formula $\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$. The compound is highly polymerized in solution.

We have observed the oxidation of Ce(III) in the presence of concentrated nitrate solutions to form a Ce(IV)-nitrate-DEHP complex. As compared to other methods of oxidation and extraction such as silver-catalyzed persulfate, ozone, $10\text{M HNO}_3\text{-KBrO}_3$, or electrolysis, this observation appears unique. We have not attempted to define the oxidation mechanism in this report, but have concentrated on these observations. We do not anticipate this approach for large-scale cerium - rare earth separation. We do, however, hope that these observations will be of value to the understanding of cerium - rare earth extraction and HDEHP chemistry.

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FIGURE LEGENDS

- fig. 1 The stripping distribution coefficients for cerium(III), cerium(IV) and promethium(III) between nitric acid and 0.25M HDEHP.
- fig. 2 The extraction distribution coefficients for cerium and promethium between 2M $\text{Al}(\text{NO}_3)_3$, 0.01M Ce(III), and 0.25M HDEHP and their subsequent stripping distribution coefficients with 2M HNO_3 .
- fig. 3 The cerium concentration in the 0.25M HDEHP organic phase as a function of the initial cerium concentration in the 2M $\text{Al}(\text{NO}_3)_3$.
- fig. 4 The infrared absorption spectra of (A) HDEHP, (B) $\text{Ce}(\text{DEHP})_3$, (C) $\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$ prepared by the oxidation of Ce(III) and (D) $\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$ prepared by the method of Peppard and Ferraro.
- fig. 5 The osmometric data for (A) $\text{CeO}_{0.5}\text{NO}_3(\text{DEHP})_2$ prepared by the oxidation of Ce(III) (closed circles) and prepared by the method of Peppard and Ferraro (open circles) in cyclohexane, and (B) $\text{Ce}(\text{DEHP})_3$ in cyclohexane.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5