

The Chemistry of Protactinium : X. A Study of the Effect of Chromium(II) on the Solvent Extraction of Protactinium(IV), Using N-Benzoyl-N-phenylhydroxylamine, Tri-n-octylamine and Thenoyltrifluoroacetone as the Extractants(Chemistry)

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ferrous ion is adsorbed on the unreduced oxide. There is no evidence for reduction to an intermediate solid phase. The results indicate that the two waves observed in the cathodic reduction of anodically formed (or air-formed) films are due to the presence of the two "phases" Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ in the as-formed films.

The Chemistry of Americium. II. The Behavior of Am(III), Am(V), and Am(VI) in Column Chromatography, with Bis(2-ethylhexyl)phosphoric Acid Used as the Extractant

Mitsuo HARA and Shin SUZUKI

Bull. Chem. Soc. Japan, **47** (1974), 635.

The behavior of Am(III), Am(V), and Am(VI) in column chromatography with bis(2-ethylhexyl)phosphoric acid(HDEHP) used as the extractant were investigated in comparison with that of Np(IV), Np(V), and Np(VI). When the solution of Am(VI) was submitted to the column chromatography, it was found that Am(VI) was rapidly reduced to Am(V) and partially to Am(III) by HDEHP, irrespective of the conditions, such as the flow rate, the acidity, and the composition and temperature of the influent. The optimum conditions for the separation of Am(V) and Am(III) and for the preparation of the Am(V) solution were established by utilizing the difference in the adsorbability on the column bed between Am(III) and Am(V). When a freshly-prepared Am(V) solution was submitted to column chromatography, it was found that Am(V) was also reduced to Am(III) as well as Am(VI) by HDEHP. The percentage of the Am(V) fraction eluted strongly depended on the conditions in the column chromatography, but it was found to be constant within the limits of experimental error under definite conditions as long as the same column was used. This fact was applied to the determination of the Am(V) content in the mixed solution of Am(III) and Am(V). The content of Am(V) decreased slowly in the nitrate, acetate, sulfate, and perchlorate solutions at lower temperatures, but it rapidly decreased in the chloride, iodide, sulfite, and hydrogen peroxide solutions even at 0°C. The content of Am(V) decreased more rapidly at higher temperatures, and the kinetic analysis showed that the reduction of Am(V) apparently followed the first-order kinetics in the acetate solutions.

The Chemistry of Protactinium. X. A Study of the Effect of Chromium(II) on the Solvent Extraction of Protactinium(IV), Using *N*-Benzoyl-*N*-phenylhydroxylamine, Tri-*n*-octylamine and Thenoyltrifluoroacetone as the Extractants

Isamu KAWASUJI and Shin SUZUKI

Bull. Chem. Soc. Japan, **47** (1974), 104.

Cr(II) has been used for reducing protactinium in microquantities to the tetravalent state and for protecting it from re-oxidation. However, the effect of Cr(II) on the extraction behavior of Pa(IV) has not been taken into account by all

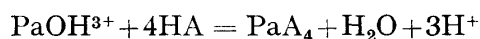
of the previous investigators. On the basis of the above facts, the influence of Cr(II) on the extraction of Pa(IV) was studied by using such extractants as BPHA, TAA, and TOA. In every case, the distribution ratio of Pa(IV) decreased with an increase in the concentration of Cr(II) in the aqueous phase. One of the most reliable explanations for the phenomena is the possibility that a multi-nuclear complex between Pa(IV) and Cr(II) or Cr(III) is formed. However, the effect of Cr(II) on the absorption spectra of Pa(IV) could not be found, and many more experiments will be necessary to explain the effect of Cr(II) on the extraction behavior of Pa(IV).

The Chemistry of Protactinium. XI. A Study of the Solvent Extraction of Protactinium(IV) Reduced with Europium(II) from a Perchloric Acid Solution, Using Thenoyltrifluoroacetone as the Extractant

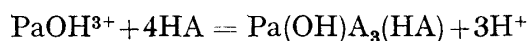
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Bull. Chem. Soc. Japan, **47** (1974), 2213.

Europium(II) was found to be an excellent reductant for reducing protactinium in microquantities to the tetravalent state. The behavior of Pa(IV) in the perchloric acid solution was investigated by the TTA-benzene extraction method. It was found that the PaOH^{3+} ion existed predominantly in a 0.03–3M perchloric acid solution at the ionic strength of 3. The reaction of TTA extraction may proceed as:



or



The distribution ratio of Pa(IV) in the system using Eu(II) as the reductant is about ten times as large as that in the system using Cr(II) as the reductant. It was considered that a non-extractable complex may be formed between Pa(IV) and Cr(III), while such a complex may not be formed when Eu(II) is used as the reductant.

A Study of Quenching of Triplets by Ferrocene

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Rate constants for quenching of several triplets by ferrocene have been determined in ethanol. Most triplets have been found to be deactivated by ferrocene, yielding no observable transient absorption. The rate constant increases with increasing triplet energy in the range 8000–17000 cm^{-1} . The quenching mechanism has been discussed, the lowest triplet level of ferrocene being estimated to be $15000 \pm 1000 \text{ cm}^{-1}$.