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THE DISTRIBUTION OF Pu(VI) AND Pu(III) IN
THENOYLTRIFLUOROACETONE-BENZENE-NITRIC ACID MIXTURES

D. L. Heisig and T. E. Hicks

February 2, 1952

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ABSTRACT

The distribution coefficients of Pu(VI) and Pu(III) have been measured as a function of the TTA, hydrogen ion, and nitrate ion concentrations in the TTA-benzene-nitric acid system. The extraction constants for Pu(VI) and Pu(III) are 1.4×10^{-2} and 2×10^{-5} , respectively.

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DISTRIBUTION OF Pu(VI)

The distribution coefficients, E , of Pu(VI) in the system thenoyltrifluoroacetone (TTA)-benzene-nitric acid have been measured, where E is defined as the ratio of the concentration of plutonium in the benzene phase to that in the aqueous phase.

The experimental procedure used was as follows: Pu(VI) was prepared and stabilized in each experiment by heating the aqueous phase containing 5×10^{-6} M plutonium of unknown valence state and 10^{-4} M potassium permanganate at 90° C before the extraction with TTA was carried out. The solutions were then cooled to room temperature and 0.01 M urea added to destroy nitrous acid if a high concentration of nitrate ion was present. One cubic centimeter each of the benzene phase and the aqueous phase containing the Pu(VI) were equilibrated in a two cubic centimeter volumetric flask in a water bath maintained at $25.0 \pm 0.1^{\circ}$ C. Fifty microliter samples were removed from the aqueous and organic phases after twenty, thirty, and sixty minutes of shaking to make certain that a stable equilibrium had been reached. These aliquots were mounted on glass cover slides and counted in an alpha counter to determine the plutonium concentration in each phase. The TTA used was synthesized by H. R. Lehman and M. W. Davis, Jr. The stock solutions were standardized spectrophotometrically with the use of the molar extraction coefficients given by

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King and Reas for TTA in wet benzene.¹

By analogy with uranyl ion^{2,3} one would expect Pu(VI) to extract into a solution of TTA in benzene by the following mechanism.

$$K_1 = \frac{(\text{PuO}_2\text{K}_2)_{\text{org.}}}{(\text{PuO}_2^{++})_{\text{aq.}}} \frac{(\text{H}^+)_{\text{aq.}}^2}{(\text{HK})_{\text{org.}}^2} = E \frac{(\text{H}^+)_{\text{aq.}}^2}{(\text{HK})_{\text{org.}}^2} \quad (2)$$

$(\text{PuO}_2^{++})_{\text{aq.}}$ in Equations (1) and (2) represents all of the Pu(VI) in the aqueous phase. If PuO_2^{++} is complexed by nitrate ion, K_1 will be a function of the nitrate ion concentration. In Equation (2) the ratio of the activity coefficients is assumed to be constant and is incorporated into K_1 .

If this is the correct mechanism and activity effects are constant, a plot of $\log E$ vs. $\log (\text{HK})_{\text{org.}}$ at any fixed hydrogen and nitrate ion concentrations should have a slope of +2.0. Similarly, a plot of $\log E$ vs. $\log (\text{H}^+)_{\text{aq.}}$ at constant nitrate ion and TTA concentrations and at constant ionic strength should have a slope of -2.0. Figures 1 and 2 from the data in Tables 1 and 2 show that the experimental slopes for these two plots are +2.0 and -2.0, respectively.

The values of K_1 in Equation (2) for each experiment have been calculated. The two groups of data in Table 1 were obtained with different TTA and plutonium stock solutions. For an ionic strength and nitrate ion concentration of 0.05, the average value of K_1 for all runs is 0.014. The corresponding value for uranyl ion measured at an ionic strength of 1.9 varies from 0.016 to 0.006 as the TTA concentration varies from 1.6 to 0.17 M.³

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Fig. 1

Variation of the Distribution Coefficient, E,
of Pu(VI) with TTA Concentration.

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Fig. 2

Variation of the Distribution Coefficient, E,
of Pu(VI) with Hydrogen Ion Concentration.

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Table 2

Variation of the Distribution Coefficient, E,
of Pu(VI) with Hydrogen Ion Concentration

Conditions: 25°C, 2×10^{-4} M KMnO_4 , 0.175 M NO_3^-

$(\text{TTA})_{\text{org.}}/(\text{TTA})_{\text{aq.}} = 52$, 0.756 M TTA in benzene initially,
0.741 M TTA in benzene at equilibrium.

Experiment Number h	HNO_3 M	LiNO_3 M	E (org./aq.)	K_1
26	0.175	0	0.24	0.013
29	0.112	0.063	0.60	0.014
28	0.080	0.095	1.06	0.012
27	0.049	0.126	2.88	0.013
Average				0.013

Pu(VI) COMPLEXING BY NITRATE ION

Since the distribution coefficient, E, will vary with the nitrate ion concentration if PuO_2^{++} is complexed by nitrate ion, the complexing constant, K_2 , for the reaction in the aqueous phase

can be calculated from the variation of E with the nitrate ion concentration. By definition

$$E = \frac{(\text{PuO}_2\text{K}_2)_{\text{org.}}}{(\text{PuO}_2^{++})_{\text{aq.}} + (\text{PuO}_2\text{NO}_3^+)_{\text{aq.}}} \quad (4)$$

It is assumed that only one nitrate ion will be complexed with each plutonyl

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ion. Belts and Michels⁴ found only a single nitrate complexing constant for uranyl ion at an ionic strength of 5.4 when the nitrate ion varied from 1.0 to 7.0 M. With the equilibrium constant from Equation (3), Equation (4) can be transformed to

$$E_0 = E \left[1 + K_2(\text{NO}_3^-) \right] \quad (5)$$

where E_0 is the distribution coefficient when no nitrate is present. From the data in Table 3, K_2 has been calculated and found to be 0.25 at an ionic strength of 4.6. K_2 has been reported to be 0.19 at an ionic strength of 8 from extraction studies with TTA by workers at Knolls Atomic Power Laboratory.⁵

Table 3

Variation of the Distribution Coefficient, E ,
of Pu(VI) with the Nitrate Ion Concentration

Conditions: 25° C, 10^{-4} M KMnO_4 , 0.01 M urea, 0.049 M HNO_3

Initial $(\text{TTA})_{\text{org.}} = 0.756$ M

Experiment Number h	LiNO_3 <u>M</u>	LiClO_4 <u>M</u>	μ	E (org./aq.)
36	0	4.53	4.6	4.11
33	1.0	3.5	4.6	3.25
35	4.5	0	4.6	2.15
34	1.0	0	1.1	2.41

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DISTRIBUTION OF Pu(III)

An attempt was made to measure the distribution coefficients of Pu(III) in the TTA-benzene-nitric acid system by methods similar to those used for Pu(VI). In the presence of TTA, Pu(III) was never stabilized in the reaction mixtures with 0.01 M ferrous perchlorate, metallic tin, or chromous acetate under N_2 in the presence of hydrochloric acid rather than nitric acid. The observed distribution coefficient in all cases increased as a function of time, probably due to the formation of Pu(IV). The distribution coefficient of Pu(IV) is of the order of 10^7 or 10^8 under these conditions so that Pu(IV) would be extracted into the organic phase almost as rapidly as it is formed. The best results were obtained by reducing the plutonium stock to Pu(III) in each reaction vessel with 0.005 M ferrous perchlorate. 0.01 M sulfamic acid was added to destroy nitrous acid if a high nitrate ion concentration was present.

At intervals of about twenty minutes, fifty microliter portions of each phase were removed and mounted on glass cover glasses for counting in an alpha counter. From a plot of counts per minute in the organic phase vs. time such as shown in Figure 3, the counts per minute in the organic phase were extrapolated back to zero time where the plutonium was presumably all in the (III) valence state. From this value and the material balance, the distribution coefficients of Pu(III) in the system were calculated. The experimental results are shown in Table 4.

The slope of a plot of $\log E$ for Pu(III) vs. $\log (HK)_{org.}$ at constant nitrate and hydrogen ion concentrations and constant ionic strength is +2.3 while that of $\log E$ vs. $\log (H^+)_{aq.}$ at constant TTA concentration is -2.6 (Figures 4 and 5). While these slopes, as well as the

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Fig. 3

Extraction of Pu(III) into 1.64 M TTA in Benzene
as a Function of Time.

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Fig. 4

Variation of the Distribution Coefficient, E, of
 Pu(III) with Hydrogen Ion Concentration.

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Fig. 5

Variation of the Distribution Coefficient, E, of
Pu(III) with TTA Concentration.

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Table 4

Variation of the Distribution Coefficient, E,
of Pu(III) with TTA and Hydrogen Ion Concentration

Conditions: 25° C, 0.005 M Fe(ClO₄)₂

Experi- ment Number H	HNO ₃ M	LiNO ₃ M	NO ₃ ⁻ M	Initial TTA in Benzene M	(TTA) org. (TTA) aq.	Equili- brium TTA in Benzene M	E (org./aq.)	K ₃ x 10 ⁵
26	0.032	0.064	0.096	1.68	58	1.65	1.7	1.3
27	0.049	0.047	0.096	1.68	58	1.65	0.57	1.5
28	0.072	0.024	0.096	1.68	58	1.65	0.20	1.7
29	0.096	0	0.096	1.68	58	1.65	0.098	2.0
30	0.032	0.064	0.096	0.60	50	0.58	0.20	3.5
31	0.032	0.064	0.096	0.85	53	0.83	0.44	2.6
32	0.032	0.064	0.096	1.28	56	1.26	0.93	1.6
33	0.032	0.064	0.096	1.68	58	1.65	1.82	1.4
Average								2.0

low extractability of plutonium, indicate that the major fraction of the plutonium is present as Pu(III), no definite conclusions concerning the mechanism of the extraction can be drawn due to the inaccuracy of the measurements. If the mechanism follows Equations (6) and (7)

$$K_3 = \frac{(\text{PuK}_3)_{\text{org.}} (\text{H}^+)_{\text{aq.}}^3}{[\text{Pu(III)}]_{\text{aq.}} (\text{HK})_{\text{org.}}^3}, \quad (7)$$

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the slopes of the above plots of $\log E$ vs. $\log (HK)_{org.}$ and $\log E$ vs. $\log (H^+)_{aq.}$ would be +3 and -3, respectively. With the assumption that the extraction of Pu(III) proceeds by Equation (6) and that all activity coefficient effects could be included as a constant in K_3 , the value of K_3 was estimated to be 2×10^{-5} in 0.1 M nitrate solutions from the data in Table 4.

Pu(III) COMPLEXING BY NITRATE ION

By observing the drop of the distribution coefficient of Pu(III) in this system with the increase in the nitrate ion concentration in the aqueous phase (Table 5), it was concluded that Pu(III) is more strongly complexed by nitrate than is Pu(VI).

Table 5

Variation of the Distribution Coefficient, E ,
of Pu(III) with Nitrate Ion Concentration

Conditions: 25°C, 0.005 M $Fe(ClO_4)_2$,

0.01 M sulfamic acid, 0.049 M HNO_3 .

1.68 M TTA in benzene initially

Experiment Number H	$Ca(NO_3)_2$ <u>M</u>	NO_3^- <u>M</u>	H^+ <u>M</u>	E (org./aq.)
13	0	0.05	0.059	0.55
36	0.95	1.95	0.059	0.05
35	1.90	3.85	0.059	0.02

The ionic strength as well as the nitrate ion concentration is a variable in this series.

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