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# Studies of the Behavior of Trivalent Uranium in an Aqueous Solution. III. Extraction from a Hydrochloric Acid Solution by Bis(*n*-butyl) Orthophosphoric Acid and by Bis-(2-ethylhexyl) Orthophosphoric Acid

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The distribution of U(III) between hydrochloric acid solutions and benzene solutions of bis-(*n*-butyl) orthophosphoric acid or cyclohexane solutions of bis(2-ethylhexyl) orthophosphoric acid has been investigated by using the uranium-237 isotope as a tracer. It has been found that the log-log plot of the distribution ratio *vs.* the concentration of dimeric organophosphoric acids, and that of the distribution ratio *vs.* the hydrogen ion concentration, always show a good linearity, with a slope of 3. This indicates that the complex-forming reaction is as follows:

$$U^{3+} + 3(HA)_2 \rightleftarrows U(HA_2)_3 + 3H^+$$

where $(HA)_2$ represents the dimeric solvent, $(HDBP)_2$ or $(HDEHP)_2$. The above results are in agreement with the conclusions reached in the cases of other trivalent actinide and lanthanide elements by other investigators.

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Several papers have been reported on U(III) because of its instability in aqueous solutions.1–4) The present authors found that U(III) is fairly stable in aqueous solutions at low acid concentrations in the absence of atmospheric oxygen.5) They studied the preparation, stability, absorption spectra, and ion-exchange behavior of U(III) in various acid solutions.5,6) The reduction of U(VI) to U(III) with liquid zinc amalgam gives a high yield within a short period of time and with a good reproducibility. Particularly in a hydrochloric acid solution, the reduction is more complete than in other media, and the stability of U(III) is also high. Its stability increases with the decrease in the acid concentration.

In this paper, the solvent-extraction behavior of U(III) in hydrochloric acid solutions will be reported on; the investigations were done by using bis(*n*-butyl) orthophosphoric acid-benzene and bis-(2-ethylhexyl) orthophosphoric acid-cyclohexane.

## Experimental

**Reagents and Apparatus.** *Uranium-237 and Hydrochloric Acid Solutions of U(VI).* The uranium-237 tracer was prepared by the conventional method6,7) after natural uranium dioxide had been irradiated for about 2 hr with 20 or 50 MeV Bremsstrahlung from the Liniac, JAERI, or the Laboratory of Nuclear Science, Tohoku University.

*Bis(2-ethylhexyl) Orthophosphoric Acid (HDEHP) and Bis(n-butyl) Orthophosphoric Acid (HDBP).* The HDEHP and HDBP were purified by the method reported by Peppard *et al.*8) The purified organophosphoric acids were dissolved with a purified solvent such as benzene or cyclohexane. The concentration of organophosphoric acid was determined by titrating it with a standard sodium hydroxide solution.

The liquid zinc amalgam was prepared by a method reported previously.5) The benzene and the other solvents were purified before use in the usual manner. All the other chemicals, such as hydrochloric acid and lithium chloride, were of an analytical grade.

The reductor and radiation measurement instruments were those described in a previous report.6)

**Procedures.** All the experiments were carried out in a plastic globe-box with an argon, nitrogen, or carbon dioxide atmosphere at 25±2°C.

Five milliliters of a uranyl chloride solution tagged with a uranium-237 tracer were taken into the reductor. A calculated quantity of lithium chloride solution was added to this to maintain the ionic strength of the total aqueous phase at 0.2, and then the total volume was adjusted to 10 m*l*. After about 10 m*l* of the liquid zinc amalgam had been added to the reductor, the U(VI) was reduced as has been described in a previous report.5) After the liquid zinc amalgam had then been

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1) K. Someya, *Z. Anorg. Allgem. Chem.*, **161**, 46 (1927).

2) C. K. Jϕrgensen, *Acta Chem. Scand.*, **10**, 1503 (1956).

3) D. C. Stewart, ANL-4812 (1952).

4) V. F. Peretrukhin, N. N. Krot and A. D. Gel'man, *Radiokhimiya*, **8**, 670 (1966).

5) A. Satō, This Bulletin, **40**, 2107 (1967).

6) A. Satō and S. Suzuki, *ibid.*, **41**, 2650 (1968).

7) E. Akatsu, T. Kuroyanagi and T. Ishimori, *Radiochim. Acta*, **2**, 1 (1963).

8) D. F. Peppard, J. R. Ferraro and G. W. Mason, *J. Inorg. Nucl. Chem.*, **7**, 231 (1958).

carefully removed from the reductor, 10 m*l* of a HDBP or HDEHP solution was added to it. Both phases were shaken with a mechanical shaker.

*Pre-equilibration.* Two portions of barren HDBP or HDEHP were, successively, placed in contact with two equal-volume portions of barren aqueous acid. The second portions of the solvent and aqueous phases were then used in the study.

Care was taken to ascertain the material balance in each case; the concentration of uranium in the aqueous phase was about $2\times10^{-3}$M.

After the separation of the two phases, a 1 m*l* aliquot of each phase was taken into a polyethylene tube. The $\gamma$-radioactivity was measured with a well-type scintillation counter, and the distribution ratio, D, was calculated.

Here, D is defined as:

$$\text{D} = \frac{\gamma\text{-activity per m}l\text{ of the org. phase}}{\gamma\text{-activity per m}l\text{ of the aq. phase}}$$

The hydrogen-ion concentration of the aqueous phase in equilibrium was determined by titration with a standard sodium hydroxide solution.

To an extent depending on the kind of mineral acid and its concentration, the reduction of U(VI) to U(III) does not proceed completely[5] and U(IV) is also present in the sample solution. Although an insoluble U(IV) compound forms between the two phases in the extraction with $(\text{HDBP})_2$ below 0.10M, it can be easily separated by the centrifugal method. The solubility of this compound increases with an increase in the HDBP concentration; about 30% of the U(IV) is extracted with a 0.25M $(\text{HDBP})_2$ - benzene solution. On the other hand, U(IV) is completely extracted into the HDEHP phase over a wide range of hydrochloric acid concentrations. Consequently, it was necessary to correct for this by the method reported previously.[6]

## Results

**Experimental Conditions.** The equilibrium of the solvent extraction with HDBP or with HDEHP was reached within about 30 sec. Therefore, a shaking time of 60 sec is recommended.

*Diluent.* As is shown in Table 1, the relative extractability of U(III) increases in the following sequence: cyclohexane>xylene>isopropyl ether>toluene>benzene. Uranium(III) is extracted to a moderate extent with HDBP, while it is very poorly extracted with HDEHP from a weak hydrochloric acid solution. On the basis of these results, we used benzene as the diluent for the HDBP extraction and cyclohexane for the HDEHP extraction.

TABLE 1. INFLUENCE OF THE DILUENT FOR THE $\text{U}^{3+}$-HDEHP AND - HDBP SYSTEM

| Diluent | Distribution ratio* | |
|---|---|---|
| | $\text{U}^{3+}$-HDEHP | $\text{U}^{3+}$-HDBP |
| Cyclohexane | 2.6 | 450 |
| Xylene | 0.8 | 36 |
| Isopropyl ether | 0.4 | 16 |
| Toluene | 0.03 | 9.8 |
| Benzene | 0 | 6.5 |

* HCl, 0.05M; $(\text{HDEHP})_2$ or $(\text{HDBP})_2$, 0.1M; U, $2\times10^{-3}$M

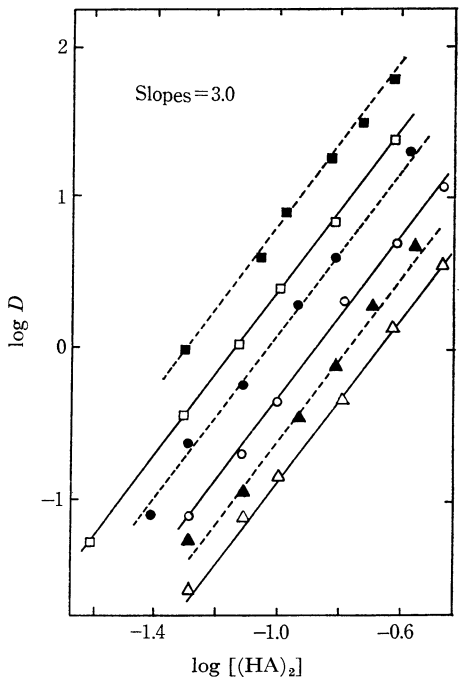

Fig. 1. Extractant dependency of the extraction o the U(III) into HDBP or HDEHP.
HDBP extraction;
---■---■---: 0.06M HCl ---●---●---: 0.1M HCl
---▲---▲---: 0.15M HCl
HDEHP extraction;
—□—□—: 0.06M HCl —○—○—: 0.1M HCl
—△—△—: 0.14M HCl

The extraction of U(IV) with HDEHP is practically complete over a wide range of hydrochloric acid concentrations. The back extraction into the aqueous phase is difficult even with high concentrations of hydrochloric acid. However, the back extraction of U(III) is complete in a hydrochloric acid solution of>2M. The above results are in good agreement with those of Peppard *et al.*,[9,10] who were concerned with the distribution coefficients of other actinide elements between HDEHP and hydrochloric acid.

**Solvent Dependence of the Distribution Ratio.** As is shown in Fig. 1, a good linear solvent dependency is seen to be directly third power over a wide range of HDBP and HDEHP concentrations for 0.06, 0.1, and 0.14M hydrochloric acid con-

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[9] D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *ibid.*, **4**, 334 (1957).

[10] D. F. Peppard, S. W. Molin and G. W. Mason, *ibid.*, **4**, 344 (1957).

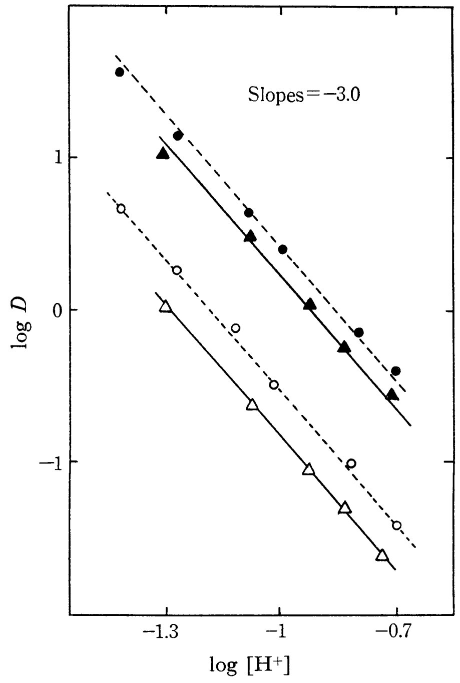

Fig. 2. Hydrogen ion dependency of the extraction of the U(III) into HDBP or HDEHP.
---○---○---: 0.05M $(HDBP)_2$, ---●---●---: 0.14M $(HDBP)_2$, —△—△—: 0.05M $(HDEHP)_2$, —▲—▲—: 0.15M $(HDEHP)_2$

centrations. Each point is the mean of six experiments, having the standard deviations of 2.3—3.8% for the HDEHP extraction and 1.7—4.2% for the HDBP extraction.

**Acid Dependence of the Distribution Ratio in a Constant-ionic-strength Medium.** The effect of the acidity of the aqueous phase was studied at the constant ionic strength of 0.2. Benzene solutions of 0.05 and 0.14M $(HDBP)_2$ and cyclohexane solutions of 0.05 and 0.15M $(HDEHP)_2$ were used for the extraction. It is clear from Fig. 2 that the log-log plot of the distribution ratio and the hydrogen ion concentration in the aqueous phase shows a linear relationship with a slope of an inversive third power. Each point is the mean of six experiments, having the standard deviations of 1.3—3.9% for the HDEHP extraction and 2.2—4.7% for the HDBP extraction.

## Discussion

It should be noted that, in the present discussion, HA is a dimer.[8,11–15] Consequently, for HDBP or HDEHP, the ionization of the extractant and the composite equilibrium are written as:

$$(HA)_2(org) \rightleftarrows H^+(aq) + H(A)_2^-(org)$$

where the subscripts (aq) and (org) refer to the aqueous and the organic phase respectively and where HA represents the organophosphoric acid solvent, HDBP or HDEHP.

Thus, the above equation becomes:

$$M^{m+}(aq) + m(HA)_2(org) \rightleftarrows M[H(A)_2]_m(org) + mH^+(aq)$$

The expression for the distribution ratio, $D$, is written as:

$$D = K_E[(HA)_2]^m(org)/[H^+]^m(aq)$$

If the temperature and the concentration of HDBP or HDEHP, or the pH, are constant in the extraction, the following equations can be obtained from the above equation:

$$\log D = \log K_E[H^+]^{-m}(aq) + m \log [(HA)_2](org)$$

and:

$$\log D = \log K_E[(HA)_2]^m(org) + m \log [H^+]^{-1}(aq)$$

From the experimental results shown in Figs. 1 and 2, the plots of log $D$ *vs.* the log of the HDBP or HDEHP concentration and the plots of log $D$ *vs.* the pH show straight lines, with a slope of 3, so it can be considered that the species extracted into the organic phase have the form of $U[H(DBP)_2]_3$ or $U[H(DEHP)_2]_3$. This indicates that the complex-forming reaction is as follows:

$$U^{3+} + 3(HDBP)_2 \rightleftarrows U[H(DBP)_2]_3 + 3H^+$$

or:

$$U^{3+} + 3(HDEHP)_2 \rightleftarrows U[H(DEHP)_2]_3 + 3H^+$$

Here, a good agreement is seen with the conclusions reached in the cases of other trivalent actinide and lanthanide elements by other investigators.[15–21]

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11) D. F. Peppard, J. R. Ferraro and G. W. Mason, *J. Inorg. Nucl. Chem.* **4**, 371 (1957).

12) D. Dyrssen, *Acta Chem. Scand.*, **11**, 1771 (1957).

13) C. J. Hardy and D. Scargill, *ibid.*, **11**, 128 (1959).

14) D. Dyrssen and L. D. Hay, *ibid.*, **14**, 1091 (1960).

15) C. F. Baes, Jr., *J. Inorg. Nucl. Chem.*, **24**, 707 (1962).

16) D. Dyrssen, *Acta Chem. Scand.*, **11**, 1277 (1957).

17) D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, *J. Inorg. Nucl. Chem.*, **7**, 276 (1958).

18) D. Dyrssen and L. D. Hay, *Acta Chem. Scand.*, **14**, 1100 (1960).

19) G. Duyckaerts, Ph. Dreze and A. Simon, *J. Inorg. Nucl. Chem.*, **13**, 332 (1960).

20) D. F. Peppard, G. W. Mason and I. Hucher, *ibid.*, **18**, 245 (1961).

21) G. W. Mason, S. Lewey and D. F. Peppard, *ibid.*, **26**, 2271 (1964).