# Extraction of Uranyl Butyrate by Organic Solvents. Distribution and Rate of Transfer in Continuous Countercurrent Spray Extraction Column

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The solvent extraction has been widely used for commercial purification of uranium compounds for production of high purity uranouranic oxide ($U_3O_8$) and uranium metal.

The distribution of uranyl nitrate between water and various organic solvents and its continuous countercurrent extraction in spray, packed, wetted-wall, and pulse columns have been studied by many workers *(1-8)*. The distribution study for this salt shows that the extraction capacity of solvents rapidly falls off with decrease in concentration and and is very poor at the dilute end.

It has been found by experiment that uranyl butyrate gives favorable distribution with a number of organic solvents, even at the dilute end.

An investigation has been carried out (*1*) to find the equilibrium distribution of uranyl butyrate between water and several organic solvents and (*2*) to study the rate of transfer in continuous countercurrent spray extraction column with some suitable solvent selected for the purpose, such as isoamyl alcohol.

## DISTRIBUTION OF URANYL BUTYRATE BETWEEN WATER AND ORGANIC SOLVENTS

**Preparation of Uranyl Butyrate Stock Solution.** Uranyl butyrate was prepared from uranyl nitrate (hexahydrate, Mallinkcrodt, analytical reagent quality). An ounce of the salt was dissolved in about 500 ml. of water and ammonium diuranate, $(NH_4)_2\ U_2O_7$, was precipitated by the addition of sufficient quantity of liquid ammonia. The precipitate was filtered, and washed free of ammonium nitrate, and then mixed with an excess of butyric acid (pure, E. Merck) to form a slurry. The slurry was dissolved in sufficient quantity of distilled water, and the solution obtained was carefully evaporated to saturation and then cooled overnight to crystallize the uranyl butyrate. Three crops of crystals were collected. The crystallized product was washed with a small amount of water and then dissolved in warm water. The pH of the solution obtained was adjusted by further addition of butyric acid and the solution was preserved in a dark place for equilibrium distribution study.

**Solvents Used.** The solvents used were methyl isobutyl ketone (supplied by Burmah-Shell, the fraction distilled at 117-18°C. was used for the distribution study); ethyl acetate (pure, boiling point, 77.15°C.); isoamyl alcohol (boiling range 128° to 132°C.); cyclohexanone (boiling range 154° to 156°C.).

**Equilibrium Procedure.** Aqueous uranyl butyrate solutions with different concentrations of uranium and equal volumes of the appropriate solvent were brought to equilibrium by periodically shaking for about 5 minutes, every 15 minutes for 1.5 hours, and were left overnight for separation of the phases. The temperatures of the samples were noted, and 10 ml. of each of the separated phases were then pipetted for analysis.

**Analysis.** The samples of aqueous phases were precipitated hot by addition of liquid ammonia with stirring and the precipitates of ammonium diuranate were filtered, dried, and ignited to $U_3O_8$ at about 850°C.

The samples of the solvent phase were treated similarly. In this case, sufficient distilled water was added and the mixture was boiled before precipitation with liquid ammonia. After settling of the precipitate, the clear supernatant solvent layer was decanted off before the actual filtration.

**Results of Distribution Study.** The data for uranyl butyrate distribution between water and four different solvents are shown in Figures 1 to 4.

The pH values of the different stock solutions used were adjusted by regulating the concentration of free butyric acid. No attempt was made to regulate the pH of the equilibrated aqueous phase.

Besides the above four solvents, extraction properties of solvents like benzene, toluene, carbon tetrachloride, ethylene dichloride, trichloroethylene, isoamyl acetate, hexyl alcohol, butyl alcohol, ethyl ether, and nitromethane were determined colorimetrically.

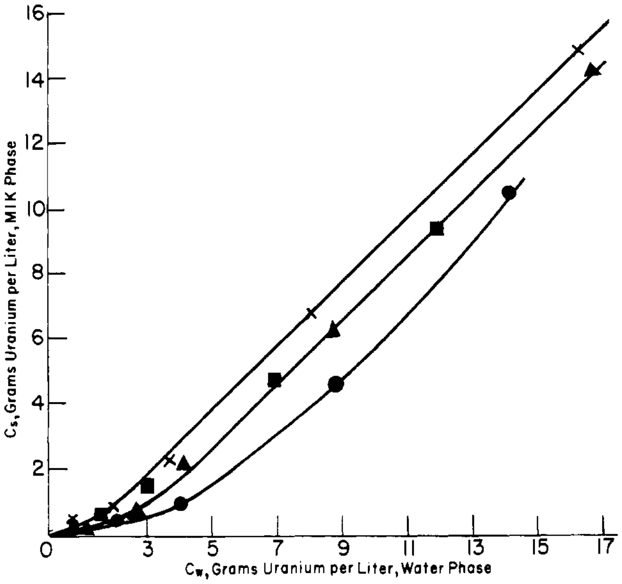

**Figure 1. Uranyl butyrate distribution between water and methy isobutyl ketone**

| | pH of Stock Solution |
|---|---|
| ● | 3.435 |
| ▲ | 3.24 |
| ■ | 2.96 |
| × | 2.64 |
| | 22-4°C. |

Of these solvents, butyl alcohol has fairly good extraction power. Ethyl ether and nitromethane also have some extraction power, and the rest are quite unsuitable.

The effect of ammonium butyrate as a salting out agent with a number of the solvents was also studied qualitatively. Isoamyl alcohol, cyclohexanone, and methyl isobutyl ketone extract uranium butyrate almost completely from an aqueous phase in the presence of sufficient ammonium butyrate.

Solvents like nitromethane and ethyl acetate give a multifold increase in the distribution ratio of uranyl butyrate in the presence of ammonium butyrate. The extraction power of toluene and isoamyl acetate is negligible even in the presence of sufficient ammonium butyrate.

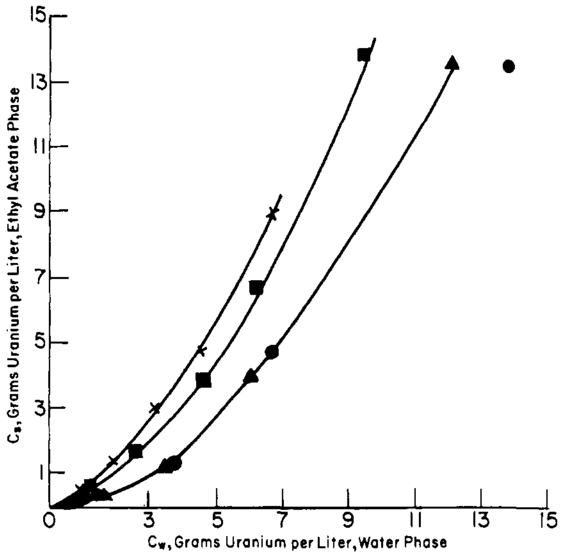

**Figure 2. Uranyl butyrate distribution between water and ethyl acetate**

pH of Stock Solution
● 3.435
▲ 3.04
■ 2.59
× 2.24
24-7 °C.

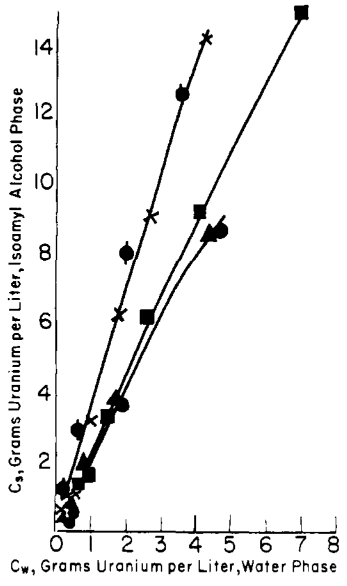

**Figure 3. Uranyl butyrate distribution between water and isoamyl alcohol**

pH of Stock Solution
● 3.58
▲ 3.16
■ 2.80
× 2.61
⧫ 2.22
27-31 °C.

## DISCUSSION OF RESULTS

The data in Figures 1 to 4 indicate that alcohols and ketones have fairly good extraction power. These results are, in general, confirmed by more qualitative studies. These latter studies also indicated that hydrocarbons and chlorinated hydrocarbons have negligible extraction power. Further, the data in the figures show that, in general, the extraction power of the solvents increases with fall of pH in the original aqueous phase—i.e., the increase in the free butyric acid concentration.

The distribution ratios, $C_s/C_w$, for the four solvents studied at approximately equal aqueous phase concentrations after equilibrium and at nearly equal pH values of the stock solution may be compared as shown in Table 1. These values have been taken from Figures 1 to 4.

Cyclohexanone was found to be the most suitable solvent of those studied, on the basis of extraction power. However, considering availability, cost, and solubility in water, isoamyl was selected for study of the rate of extraction of uranyl butyrate in a continuous spray tower.

## RATE OF EXTRACTION OF URANYL BUTYRATE BY ISOAMYL ALCOHOL IN CONTINUOUS COUNTERCURRENT SPRAY TOWER

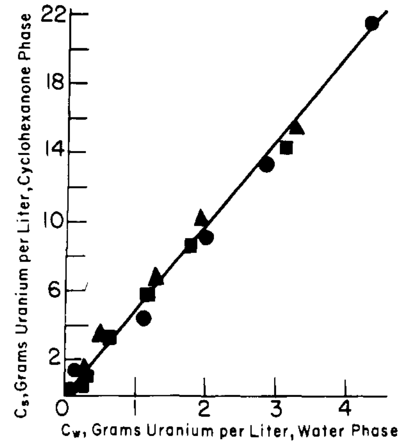

**Figure 4. Uranyl butyrate distribution between water and cyclohexanone**

pH of Stock Solution
● 2.80
▲ 2.61
■ 2.21
30-3 °C.

A solution of uranyl butyrate containing an equimolar quantity of ammonium butyrate was prepared by adding butyric acid, in excess, to the filtered and washed precipitate of ammonium diuranate which was obtained by the addition of liquid ammonia to a uranyl nitrate solution.

No attempt was made to separate the uranyl butyrate from ammonium butyrate by crystallization, as was done during

**Table I. Comparison of Distribution Ratios for Four Different Solvents**

| Solvent Used | pH of Stock Soln. | Concn. in Equilibrated Aqueous Phase of Uranium, Grams per Liter, $C_w$ | Distribution Ratio, $C_s/C_w$ |
|---|---|---|---|
| Methyl isobutyl ketone | 2.64 | 5.0 | 0.68 |
| Ethyl acetate | 2.59 | 5.0 | 0.90 |
| Isoamyl alcohol | 2.61 | 4.50 | 3.33 |
| Cyclohexanone | 2.61 | 5.0 | 5.0 |

the distribution study. Because the presence of a small amount of ammonium butyrate (equimolar with respect to uranyl butyrate) will have some effect on the distribution ratio of uranyl butyrate, separate series of equilibrium data were determined with each different solution of uranyl butyrate used in the mass transfer study. The pH values of the aqueous solutions were adjusted with free butyric acid.

The distribution data are shown in Figure 5.

The presence of a small amount of ammonium butyrate actually improves the extraction power of the solvent as shown in Table II.

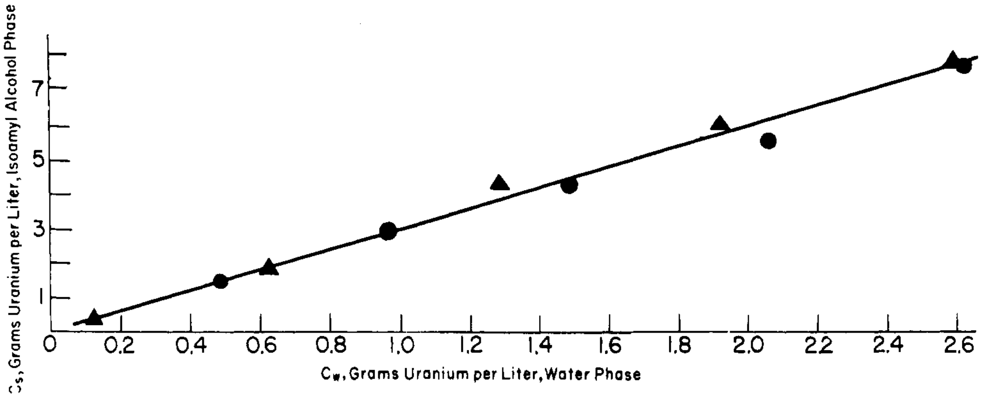

**Figure 5. Distribution of uranyl butyrate between water and isoamyl alcohol in presence of ammonium butyrate**

pH of Stock Solution
● 3.35
▲ 3.08
31-32°C.

## EXTRACTION EQUIPMENT

A diagrammatic sketch of the apparatus used is shown in Figure 6. The tower was constructed of borosilicate glass 1.5 inches in inside diameter and 5 feet high. It was built of five individual glass sections joined together by stainless steel flanges. The 5-gallon feed vessels, receiving tanks, 10-gallon overhead tanks, pipe lines, and regulating cocks were all made of stainless steel. Two glass rotameters were used to meter the flow of liquids into the column proper. The liquids entered the column through two stainless steel distributors, each having 22 perforations 1/16 inch in diameter.

**Table II. Effect of Ammonium Butyrate on Extraction**

| Temp., °C. | pH of Stock Soln. | Concn. of Ammonium Butyrate, Gram Mole/Gram Mole Uranyl Butyrate in Original Aqueous Phase | Concn. of Uranium Grams/Liter, in Equilibrated Aqueous Phase | Distribution Ratio, Read from Figures 3 and 5 |
|---|---|---|---|---|
| 28 | 3.16 | Nil | 1.0 | 2.45 |
| 28 | 3.16 | Nil | 2.0 | 2.25 |
| 32 | 3.08 | 1.0 | 1.0 | 3.25 |
| 32 | 3.08 | 1.0 | 2.0 | 3.10 |
| 31 | 3.35 | 1.0 | 1.0 | 3.05 |
| 31 | 3.35 | 1.0 | 2.0 | 2.85 |

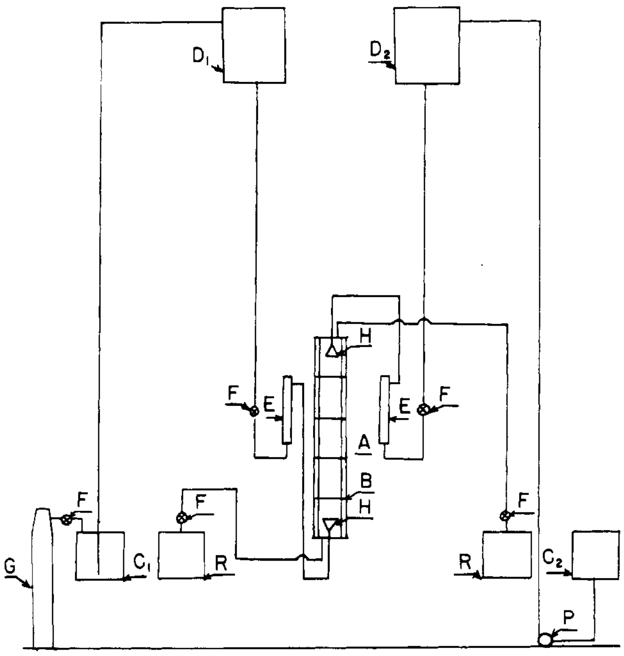

**Figure 6. Extraction equipment**

*A*. Tower
*B*. Flanges
$C_1$,$C_2$. Feed vessels
$D_1$,$D_2$. Overhead tanks
*E*. Rotameters
*F*. Regulating cocks
*G*. Gas cylinder
*H*. Distributors
*P*. Pump
*R*. Receiving tanks

## EXPERIMENTAL PROCEDURE

About 5 gallons of uranyl butyrate solution in aqueous phase containing about 10 grams of uranium per liter with equimolar amount of ammonium butyrate were prepared. The pH of the solution was adjusted by the addition of free butyric acid. This solution was fed in a feed vessel, $C_1$, whence it was pumped into the overhead tank, $D_1$. About 5 gallons of isoamyl alcohol were similarly fed into the other vessel, $C_2$, and thence into the overhead tank, $D_2$, through the action of compressed nitrogen. The phase to be main-

**Table III. System: Isoamyl Alcohol-Uranyl Butyrate-Water**
**Temperature = 30° to 32° C.**
**Column diameter = 1.5 inches, inside diameter**
**Column height = 5 feet**
**Effective column volume = 1566 ml. (54 inches of column).**

| Series | pH of Original Aqueous Phase | Phase Dispersed | Flow Rates, Cm./Min. $L_W$ | $L_S$ | Uranium Concentration, Grams/Liter Aqueous inlet, $C_{W_2}$ | Solvent outlet, $C_{S_2}$ | Aqueous outlet, $C_{W_1}$ | Solvent inlet, $C_{S_1}$ | N = Grams Uranium/Minute, Transferred, Based on Aqueous Phase | Solvent Phase | $N_{av}$, Grams Uranium/Min. | $K_{OV,W}{}^{a}$ 1/Min. | $H.T.U_{OV,W}$ Cm. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 3.35 | Isoamyl alcohol | 4.55 | 12.5 | 9.64 | 3.54 | 2.46 | 0.00 | 0.372 | 0.505 | 0.439 | 0.0579 | 78.6 |
| | | | 7.67 | 12.5 | 9.64 | 5.13 | 2.89 | 0.00 | 0.590 | 0.731 | 0.661 | 0.0840 | 91.3 |
| | | | 11.05 | 12.5 | 9.64 | 7.30 | 3.08 | 0.00 | 0.826 | 1.038 | 0.932 | 0.1210 | 91.5 |
| | | | 16.00 | 12.5 | 9.64 | 12.92 | 3.90 | 0.00 | 1.042 | 1.840 | 1.441 | 0.1930 | 83.0 |
| | | Water | 4.55 | 12.5 | 9.64 | 2.19 | 2.58 | 0.00 | 0.367 | 0.312 | 0.340 | 0.0424 | 107.5 |
| | | | 7.67 | 12.5 | 9.64 | 5.44 | 2.80 | 0.00 | 0.598 | 0.774 | 0.686 | 0.0893 | 86.0 |
| | | | 11.05 | 12.5 | 9.64 | 7.03 | 2.90 | 0.00 | 0.848 | 1.000 | 0.924 | 0.1220 | 90.6 |
| | | | 14.72 | 12.5 | 9.64 | 9.40 | 2.98 | 0.00 | 1.116 | 1.332 | 1.224 | 0.1720 | 85.6 |
| | | | 18.70 | 12.5 | 9.64 | 12.30 | 3.40 | 0.00 | 1.330 | 1.745 | 1.538 | 0.2205 | 84.8 |
| | | | 11.05 | 21.1 | 9.64 | 4.25 | 2.40 | 0.00 | 0.910 | 1.020 | 0.965 | 0.1300 | 85.0 |
| B | 3.08 | Water | 2.25 | 12.5 | 10.40 | 2.00 | 2.10 | 0.00 | 0.212 | 0.284 | 0.248 | 0.0319 | 70.7 |
| | | | 4.05 | 12.5 | 10.40 | 2.96 | 2.12 | 0.00 | 0.382 | 0.420 | 0.401 | 0.0524 | 77.3 |
| | | | 8.00 | 12.5 | 10.40 | 6.24 | 2.66 | 0.00 | 0.705 | 0.889 | 0.797 | 0.1020 | 78.5 |
| | | | 12.50 | 12.5 | 10.40 | 10.95 | 3.36 | 0.00 | 1.000 | 1.560 | 1.280 | 0.1675 | 74.5 |
| | | | 10.35 | 12.5 | 10.40 | 9.00 | 3.28 | 0.00 | 0.838 | 1.278 | 1.058 | 0.1320 | 78.5 |
| | | | 10.35 | 24.3 | 10.40 | 4.50 | 1.75 | 0.00 | 1.018 | 1.245 | 1.132 | 0.1640 | 63.0 |
| | | | 10.35 | 17.9 | 10.40 | 6.02 | 2.51 | 0.00 | 0.930 | 1.228 | 1.079 | 0.1405 | 73.6 |
| | | | 10.35 | 17.9 | 10.40 | 6.20 | 2.55 | 0.00 | 0.925 | 1.262 | 1.094 | 0.1425 | 72.6 |

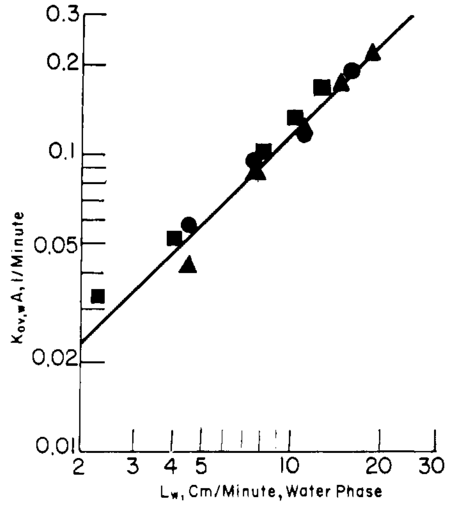

**Figure 7. Rate coefficient vs. water phase velocity for both water and solvent phases dispersed, at varying pH values of stock solutions**

| | Phase Dispersed | pH of Stock Solution |
|---|---|---|
| ● | Alcohol | 3.35 |
| ▲ | Water | 3.35 |
| ■ | Water | 3.08 |
| | Alcohol phase rate | 12.5 cm./minute |

tained continuous was then allowed to enter the column at a predetermined rate with the solvent phase outlet cock open (to drive out the air inside the column) and the water phase outlet cock closed. When the column was almost full of the continuous phase, the dispersed phase was run into the column at the desired rate. The outlet cocks were then regulated to maintain the solvent water interface at a fixed position very near to the continuous phase inlet distributor.

When the continuous phase in the column had changed by about 2 to 2.5 times, samples of outlet solvent and aqueous phases were taken. The flow rate of one of the phases was then changed regularly, keeping that of the other phase constant, and in this way, several runs were made. The samples were then analyzed for uranium content.

## RESULTS

The over-all rate coefficient $K_{ov,w}{}^{a}$, based on water phase was calculated from the equation,

$$K_{ov,w}{}^{a} = \frac{N_{av}}{V \Delta C_m}$$

where

$$N_{av} = \frac{\text{grams of uranium transferred between phases}}{\text{minute}}$$

average value

$V$ = effective column volume, liters

$$\Delta C_m = \text{log mean driving force, } \frac{(C_{w_2} - C_{w_2}^*) - (C_{w_1} - C_{w_1}^*)}{\ln \dfrac{C_{w_2} - C_{w_2}^*}{C_{w_1} - C_{w_1}^*}}$$

$K_{ov,w}{}^{a}$ = over-all rate coefficient based on water phase, $\frac{1}{\text{minute}}$

Height of an over-all transfer unit ($H.T.U_{ov,w}$) was calculated by the equation

$$H.T.U_{ov,w} = \frac{L_w}{K_{ov,w}{}^{a}}$$

where

$L_W$ = velocity of water flow, based on column cross section, cm./minute

The results are tabulated in Table III and plotted in Figures 7 to 9.

From Figure 7, it is seen that for both the water and the solvent phases dispersed and with the different pH values of the stock solution, the rate coefficient, $K_{OV,W}{}^a$, is directly proportional to the water phase velocity, $L_W^{1.0}$.

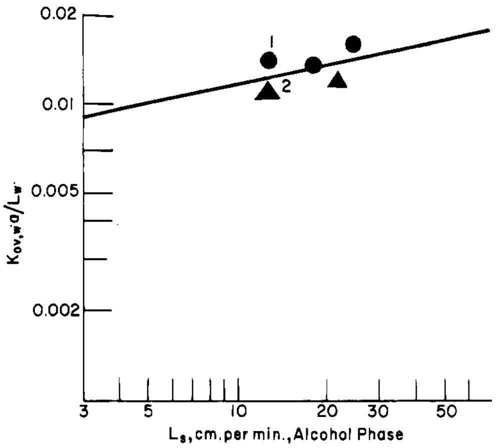

Figure 8. Rate coefficient vs. water phase velocity for both water and solvent phases dispersed, at varying pH values of stock solutions

▲ pH 3.35
● pH 3.08
1 = mean of 5 points
2 = mean of 9 points

From Figure 8, the results may be represented by the following approximate relationship for both the phases dispersed

$$K_{OV,W}{}^a = 0.007\, L_W^{1.0}\, L_S^{0.225}$$

Again, for both the phases dispersed, H.T.U.$_{OV,W}$ was found to be slightly influenced by the pH values of the stock solution and practically independent of the flow ratio as shown in Figure 9.

## DISCUSSION

From the material balance, it is found that all of the deviations between the values of the $N$, calculated from the two phases as shown in Table III, differ in the same direction except for one run. Rather high deviation on the material balance may be due to nonattainment of a perfectly steady condition in the column and to slight changes in the volume of phases due to mutual saturation and to solute transfer, for which no allowance has been made. For this deviation, an average value of $N$, based on both the phases, has been used to calculate the rate coefficients and the H.T.U. values.

From the study it appears that major resistance to mass transfer in the system lies in the aqueous phase and therefore for efficient extraction of uranyl butyrate the water phase should be dispersed.

The H.T.U.$_{OV,W}$ values, obtained here (63 to 107 cm.) may be compared with H.T.U$_{OV,ether}$ for the uranyl nitrate-diethyl ether-water system as reported by Jodra, Luina, and Oroz (*3*). In their system, where the distribution is favorable for the water phase—unlike the present system studied—the values of H.T.U$_{OV,ether}$ for the spray tower were found to lie within 47.2 to 344 cm., depending on the phase dispersed and the flow conditions.

From qualitative experiments with thorium nitrate solution, it was found that the thorium hydroxide formed by the addition of liquid ammonia is practically insoluble in butyric acid solution, unlike uranium under the same conditions. Similar experiments with cerrous nitrate show that the precipitate obtained after addition of ammonia, when treated with butyric acid, is dissolved in the form of butyrate, which is but slightly extracted by isoamyl alcohol for very low concentration of uranium in the aqueous phase. These qualitative experiments may suggest a method of separation or uranium from thorium and cerium salts.

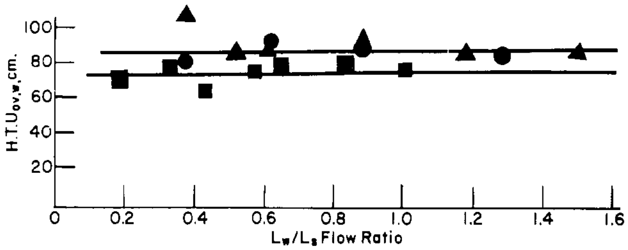

Figure 9. H.T.O.$_{OV,W}$ values vs. flow ratio, at varying pH values, for both water and solvent phases dispersed

The results of the distribution study show that isoamyl alcohol has fairly good extraction power for uranyl butyrate.

## NOMENCLATURE

$C_W$ = concentration of uranium, grams per liter in equilibrated aqueous phase
$C_S$ = concentration of uranium, grams per liter, in equilibrated organic phase
$C_W^*$ = concentration of uranium, grams per liter, of an aqueous phase in equilibrium with solvent phase
$K_{OV,W}{}^a$ = over-all rate coefficient, based on water phase, 1/minute
$N_{av}$ = grams of uranium transferred between phases per minute, average value
$V$ = effective column volume, liters
$\Delta C_m$ = log mean driving force, expressed mathematically as

$$\frac{(C_{W_2} - C_{W_2}^*) - (C_{W_1} - C_{W_1}^*)}{\ln \dfrac{C_{W_2} - C_{W_2}^*}{C_{W_1} - C_{W_1}^*}}$$

$L_W$ = superficial velocity of water flow based on column cross section, cm. per minute
$L_S$ = superficial velocity of solvent flow, based on column cross section, cm. per minute
H.T.U$_{OV,W}$ = height of over-all transfer unit, based on water phase, cm. Subscripts 1 and 2 refer to the bottom and top sections of the tower, respectively

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