아세틸아세톤과 트리부틸인산의 도데칸용액에 의한 우라늄의 용매추출

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Solvent Extraction of Uranium with Acetylacetone and Tri-*n*-Butyl Phosphate in *n*-Dodecane

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요 약. 도데칸에 녹인 아세틸아세톤과 트리부틸인산으로 묽은 질산우라닐수용액에서 우라늄(VI)을 추출했다. pH 1 이상에서 이 혼합추출제의 상승적 효과가 관측되었다. 추출되는 화학종은 1:2:1 및 1:2:2 우라닐-아세틸 아세톤-트리부틸 인산착물이다. 이들 반응의 추출정수들을 측정하였다.

ABSTRACT. Uranium (VI) was extracted from dilute aqueous solutions of uranyl nitrate with acetylacetone and tri-*n*-butyl phosphate in *n*-dodecane. Synergistic effect was observed with the mixed reagents above pH 1. The species extracted are the 1:2:1 and the 1:2:2 uranyl-AA-TBP complexes. The extraction constants for these reactions have been determined.

INTRODUCTION

Acetylacetone(HAA) is a simple β-diketone. A weak acid with $pKa=8.2$[1], HAA has long been used as a chelating agent for many metals.[2] It is quite soluble in water and its distribution coefficient is $E=5.95$ for benzene/water system.[3] Because of its solubility in water, HAA has not been so widely used as, *e.g.*, thenoyltrifluoroacetone in solvent extraction studies of metals. In the present study, the synergistic extraction of uranium(VI) with tributyl phosphate (TBP)-HAA mixed extractants has been detrmined.

EXPERIMENTAL

HAA and TBP were both G.R. grade and dodecane was technical grade from Benz Ltd., West Germany. Uranyl nitrate was prepared by reacting UO_2 powder with nitric acid, followed by crystallization of the salt as $UO_2(NO_3)_2 \cdot 6H_2O$. HAA and TBP were dissolved in dodecane and uranyl nitrate in water. Equal volumes of organic and aqueous phases were equilibrated in 100 m*l* separatory funnels by vigorous shaking for several minutes. Equilibrium temperature was 25 °C or ambient. pH measurements were made by using a Corning Model 130 pH meter. The concentrations of uranium were determined by the method of Davies and Gray.[4] For analysis the uranium in the organic phase was reextracted using 0.1 M HNO_3 solutions.

RESULTS AND DISCUSSION

Uranyl Nitrate/HAA-TBP System. Neither HAA nor TBP extracts appreciable amounts of UO_2^{2+} if used separately but, when the two are mixed, a synergistic enhancement of extraction is observed (*Fig.* 1). Solutions of HAA-
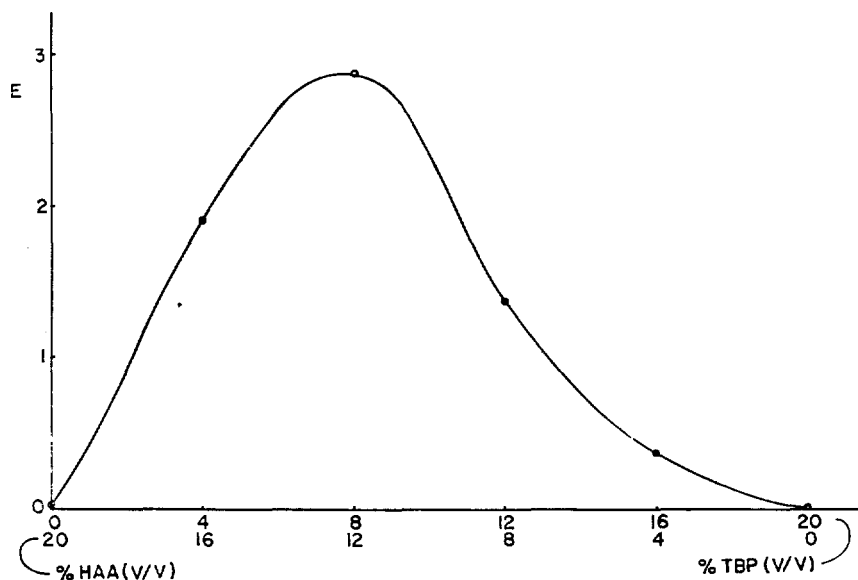
Fig. 1. Extraction of $6.0 \times 10^{-3} M$ uranyl nitrate with equal volumes of HAA-TBP mixtures in dodecane. Equilibrium pH is 1.8.

TBP mixed extractants with a total concentration of 20 % (V/V) in dodecane but varying ratios of the two were used as the organic phase. The distribution of uranium between the organic and the aqueous phases at equilibrium was plotted as a function of the concentration ratios of the two extractants.

When $6.0 \times 10^{-3} M$ uranyl nitrate solution is extracted with 20 % HAA in dodecane, the distribution coefficient is very small ($E=0.04$). Twenty percent TBP solution also gives a negligible distribution coefficient ($E=0.01$) in extracting the same uranyl solution. Thus, under the present experimental conditions, neither HAA nor TBP solution alone can extract uranium from aqueous solutions. However, the HAA-TBP mixed solutions resulted in large increase of the distribution coefficient. The value of E reaches its maximum (2.9) at about HAA: TBP=12.5:7.5 (V/V). On molar basis, this is about HAA: TBP=4:1. Thus, maximum extraction is obtained when the molar ratio of HAA/TBP is 4:1 initially in the organic

phase. TBP is practically insoluble in water but some HAA goes into aqueous phase. Therefore, the actual ratio of the two in the organic phase is less than 4:1 and the species extracted may be shown as $UO_2(AA)_2 x TBP$ with $x>0.5$. This mixed complex would be more hydrophobic than the species formed from each extractant alone.

Uranyl ion generally has coordination number 6. The AA^- anion formed from HAA by acid dissociation exists in enolate form and coordinates as bidentate. The remaining coordination positions are all or partly filled with TBP. Organic coordination-unsaturated (hydrated) complexs are rather hydrophilic. When such complexes become more coordination-saturated by, *e. g.*, forming TBP adduct, they become more hydrophobic and, therefore, more soluble (extractable) in organic solvents. Batzar[5] *et al.* reported the formula $UO_2(AA)_2$ TBP($x=$ 1) for this complex obtained under somewhat different conditions.

Compositions of the Extracted Species in

Organic Phase. The distribution equilibria involved in the extraction of uranium(VI) with HAA-TBP mixed reagents may be represented as

$$UO_{2aq}^{2+}+2HAA_{org}+xTBP_{org}$$
$$\rightleftharpoons UO_2(AA)_2xTBP_{org}+2H_{aq}^+ \quad (1)$$
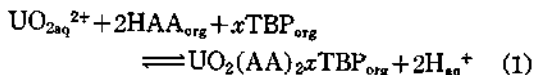
$$K_{ex}=\frac{[UO_2(AA)_2xTBP]_{org}\cdot[H^+]_{aq}^2}{[UO_2^{2+}]_{aq}[HAA]_{org}^2[TBP)_{org}^x} \quad (2)$$

$$=\frac{E\cdot[H^+]_{aq}^2}{[HAA]_{org}^2[TBP]_{org}^x} \quad (3)$$

$$logE=logK_{ex}+2log[HAA]_{org}$$
$$+xlog[TBP]_{org}+2pH \quad (4)$$

If pH and HAA concentration are kept constant, linear relationship would be obtained between $logE$ and $log[TBP]$.

Table 1 shows the variation of E with the initial TBP concentrations in the organic phase. The equilibrium pH was 1.8.

When $logE$ was plotted against $log[TBP]$, an approximately straight line with a slope about 1.5 was obtained. This is an indication that both the 1:2:1 and the 1:2:2 uranyl-AA-TBP mixed complexes are formed in the organic phase. The following reactions take place in the extraction process.
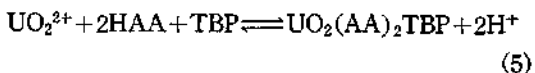
$$UO_2^{2+}+2HAA+TBP\rightleftharpoons UO_2(AA)_2TBP+2H^+$$
$$\quad (5)$$

$$UO_2^{2+}+2HAA+2TBP$$

Table 1. Uranium distribution coeffcient E as a function of TBP concentration. The initial concentrations of HAA and uranyl nitrate are 0.50 M and 0.011 M, respectively (pH=1.8).

[TBP], M	E
0.046	0.20
0.091	0.57
0.19	1.8
0.36	4.8
0.72	11.2

$$\rightleftharpoons UO_2(AA)_2(TBP)_2+2H^+ \quad (6)$$

For simplicity, the subscripts aq and org are omitted. The extraction constants for these reactions are expressed as

$$K_{1,ex}=\frac{[UO_2(AA)_2TBP][H^+]^2}{[UO_2^{2+}][HAA]^2[TBP]} \quad (7)$$

$$K_{2,ex}=\frac{[UO_2(AA)_2(TBP)_2][H^+]^2}{[UO_2^{2+}][HAA]^2[TBP]^2} \quad (8)$$

Some HAA passes into the aqueous phase and may form uranyl-AA complexes. The distribution coefficient E is then given by

$$E=\frac{[UO_2(AA)_2(TBP)]+[UO_2(AA)_2(TBP)_2]}{[UO_2^{2+}]+[UO_2AA^-]+[UO_2(AA)_2]}$$
$$\quad (9)$$

From eqs. 7, 8, and 9

$$E=\frac{[HAA]^2\{K_{1,ex}[TBP]+K_{2,ex}[TBP]^2\}}{[H^+]^2\{1+\beta_1[AA^-]+\beta_2[AA^-]^2\}} \quad (10)$$

where β_1 and β_2 are the cumulative formation constants of the uranyl-AA complexes.

Assuming that Rydberg's value[3] of E for HAA applies here and taking the protonation and the uranyl complex formation constants of acetylacetone[1], and using the initial reaction conditions and the equilibrium pH, the acetylacetonate ion concentration in the aqueous phase was estimated. The values of the extraction constants were determined graphically using eq. 10. In *Fig*.2, the intercept and slope are 2.8 and 38, respectively; from these, $K_{1,ex}=1.0\times10^{-2}$ and $K_{2,ex}=1.3\times10^{-1}$. The deviation of the high points from the straight line in *Fig*.2 is probably caused by polymerization of TBP in high TBP concentrations. Dimerization of TBP occurs to a considerable extent in n-hexane. [6]

From eqs. 7 and 8 and these values of the extraction constants, $K=[UO_2(AA)_2(TBP)_2]/[UO_2(AA)_2TBP]/[TBP]=K_{2,ex}/K_{1,ex}=13$. The following examples illustrate the significance

of these results. When the initial TBP concentration is 0.077 M, 32 % of total uranium is extracted and the organic phase contains equal amount of the 1:2:1 and the 1:2:2 U-AA-TBP complexes. If the initial TBP concentration is 0.13M, half of the uranium is extracted and the 1:2:2/1:2:1 complex ratio is 1.7. If the initial TBP concentration is 0.50 M, 88 % of uranium is extracted and the 1:2:2/1:2:1 ratio is 6.5. Thus, increasing TBP concentration produces more of the higher complex and increases the extraction.

Effect of Acidity on the Extraction. *Figs.* 3 and 4 show the effect of acidity on the extraction. The initial concentration ratios of the two reagents in the organic phase approximately correspond to the maximum in *Fig.* 1. This organic solution was equilibrated with the aqueous phase where the initial uranyl nitrate concentration was 0.041 M(*Fig.* 3). Nitric acid was used for the high acidity region. In *Fig.* 4, the initial concentration ratio of the two reagents in the organic phase remains unchanged but the concentration levels are higher. The resulting log$E$ *vs.* pH curves exhibit three different regions(A, B, and C in *Figs.* 3 and 4) depending on the pH.

Region A (TBP region): In this region the nitric acid concentration increases as one goes left. In such high acidity, the weak acid HAA remains unionized even in the presence of complexing metal ions. HAA does not react with uranyl ion and therefore does not participate in the extraction process. In this region, the extraction proceeds according to the reaction[7]

$$UO_2^{2+}+2NO_3^-+2TBP \rightleftharpoons UO_2(NO_3)_22TBP$$
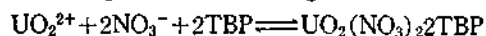
Here the hydrogen ion concentration is practically equal to the nitrate ion concentration and the ideal slope of the ascending part of the curve is −2. The leveling-off of the curve on going further to the left is caused by
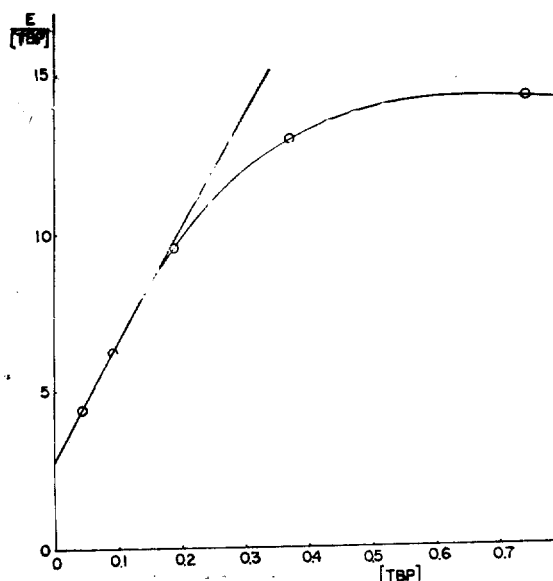

Fig. 2. Variation of $E/[TBP]$ with $[TBP]$. The data in *Table* 1 were used.
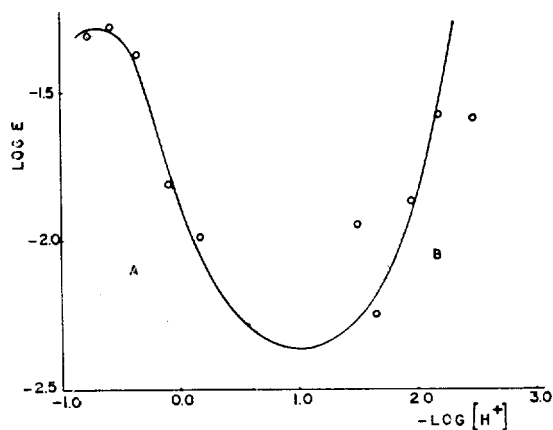

Fig. 3. Effect of acidity on extraction. The initial concentrations are: HAA, 0.100M; TBP, 0.027M; and uranyl nitrate, 0.041 M. The acidity was controlled by HNO_3 and NaOH.

the competition of HNO_3 with UO_2^{2+} ion for TBP molecules or by the formation of the unextractable complex $HUO_2(NO_3)_3$.[8]

Region B (Chelate–synergistic region): The pH was adjusted with NaOH in this region. Acid dissociation of HAA molecules takes place more readily as the pH is raised. A chelate
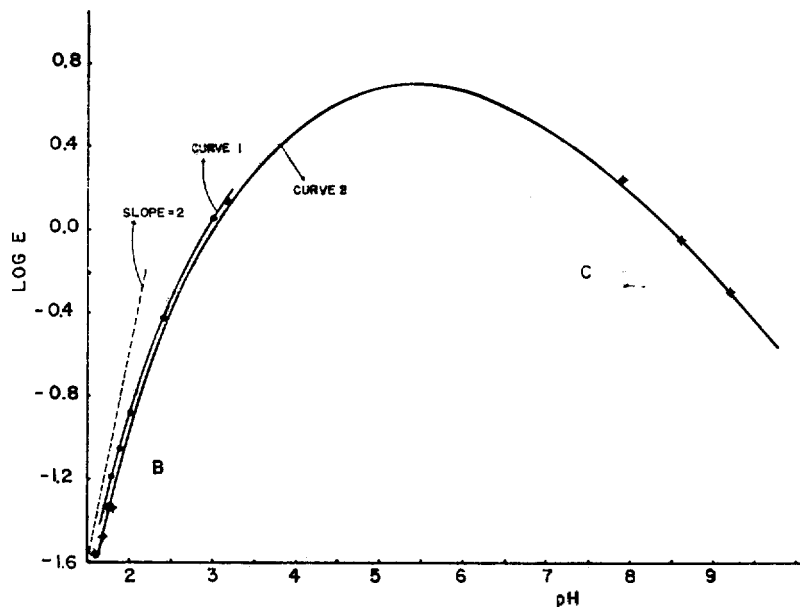
Fig. 4. Effect of pH on extraction. The initial concentrations are: uranyl nitrate, 0.048 M for curve 1, 0.047 M for curve 2; TBP, 0.100 M; and HAA, 0.400 M. pH adjusted with NaOH and HNO₃.

species $UO_2(AA)_2$ is produced. The TBP molecules form adducts with this coordination-unsaturated species. As a result, the extractable mixed complexes are formed.

If the concentrations of the two reagents are kept constant, the $\log E$ *vs.* pH plot will give a straight line with a slope of 2 (Eq. 4). *Figs.* 3 and 4 show that this ideal situation is approached in this region. This limiting slope of the ascending part of the plot shows that two molecules of HAA participate in the extraction as indicated above. The influences of regions A and B cause a minimum E region around pH 1.

Region C (Anionic-hydrolytic region): As the pH is further increased, anionic complexes such as $UO_2(AA)_2(OH)^-$ are formed in the aqueous phase. Such complexes are unextractable and the E value decreases with pH. Thus, the regions B and C create a maximum E region, where maximum amount of

$UO_2(AA)_2$ is produced and these form the TBP adducts which are extracted.

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