Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 30 June 2001

To cite this Article Pierce, Robert A. , Thompson, Major C. and Ray, Robert J.(2001) 'SOLUBILITY LIMITS OF DIBUTYL PHOSPHORIC ACID IN URANIUM-NITRIC ACID SOLUTIONS', Separation Science and Technology, 36: 5, 767 — 783
To link to this Article: DOI: 10.1081/SS-100103619
URL: http://dx.doi.org/10.1081/SS-100103619

SEPARATION SCIENCE AND TECHNOLOGY, 36(5&6), 767–783 (2001)

SOLUBILITY LIMITS OF DIBUTYL PHOSPHORIC ACID IN URANIUM-NITRIC ACID SOLUTIONS

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ABSTRACT

The Savannah River Site has enriched uranium (EU) solution that has been stored since being purified in its solvent extraction processes. The concentrations in solution are approximately 25mM U and 0.1 M nitric acid. Residual tributylphosphate in solution has slowly hydrolyzed to form dibutyl phosphoric acid (HDBP) at concentrations averaging 0.14-0.2450 mM. Dibutyl phosphoric acid, in turn, is in equilibrium with $(HDBP)_2$ and DBP^-. Uranium can form compounds with the dibutylphosphate ion (DBP^-) which have limited solubility, thereby creating a nuclear criticality safety issue.

Literature reports and earlier SRTC tests have shown that it is feasible to precipitate U-DBP solid during the storage and processing of EU solutions. As a result, a series of solubility experiments were run at nitric acid concentrations from 0-4.0 M HNO_3, uranium at 0-378 mM, and temperatures from 0-30°C. The data show temperature and HNO_3 concentration dependence consistent with what would be expected. With respect to uranium concentration, U-DBP solubility passes through a minimum between 25 and 50 mM U at the HNO_3 concentrations and temperatures studied.

However, the minimum shows a slight shift toward lower uranium concentrations at lower HNO_3 concentrations. The shifts in solubility are strongly dependent upon the overall ionic strength of the solution.

These data also reveal a shift to higher DBP solubility above 0.5 M HNO_3 for both 25 mM and 50 mM uranium solutions. Analysis of U-DBP solids from the tests identified distinct differences between precipitates from $<$0.5 M solutions and those from $>$4 M acid. Analyses identified $UO_2(DBP)_2$ as the dominant compound present at low HNO_3 concentrations in accordance with literature reports. As the acid concentration increases, the crystalline $UO_2(DBP)_2$ shows molecular substitutions and an increase in amorphous content.

INTRODUCTION

The Savannah River Site has enriched uranium (EU) solution which has been stored for almost 10 years since being purified in the second uranium cycle solvent extraction process. The concentrations in solution are approximately 25 mM U and 0.1 M nitric acid. After reprocessing, the solution contained about 200 μg of dissolved tributyl phosphate (TBP) per gram of solution and a thin film of 7.5 vol.% TBP in n-paraffin diluent floating on top of the solution. The dissolved TBP has slowly hydrolyzed to dibutyl phosphoric acid (HDBP) giving an average concentration of HDBP in solution of 0.14-0.24 mM. The hydrolysis reaction is slow at ambient temperature and low HNO_3 concentration so that all the TBP has not yet hydrolyzed. Uranium is known to form compounds with the dibutyl phosphate ion (DBP^-), a compound in equilibrium with HDBP, which have limited solubility.[1-7] Baldwin and Higgins measured the molecular weight of $UO_2(DBP)_2$ to be $>$10,000 demonstrating that the compound is highly associated or polymeric. SRTC tests have shown that $UO_2(DBP)_2$ solids will precipitate at concentrations potentially attainable during storage and processing of enriched uranium solutions.

The solubility product of $UO_2(DBP)_2$ has been reported to be 5.6×10^{-4} in 0.2 M HNO_3 and a solubility product constant was calculated[2] to be 6.1×10^{-11}. Previous unpublished studies at SRTC showed that at ambient temperature U did not precipitate from 25 mM U 0.1 M HNO_3 solutions with 0.48 mM DBP solution, but did precipitate when the concentration was 0.60 mM DBP solution.[5] Precipitation represents a nuclear criticality concern. A better understanding of the solubility limits for the U-HNO_3-HDBP system is needed to better understand the risks associated with solution storage, and the methods for mitigating potential hazards.

The solubility of $UO_2(DBP)_2$ was approached from two directions under a range of conditions that involved varying temperature and the concentrations of

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nitric acid, total DBP, and uranium. Total DBP represents the sum of all DBP equilibrium products in solution. The first approach involved preparing nitric acid solutions with sufficient uranium and HDBP to eventually cause precipitation and come to equilibrium. The second approach placed excess $UO_2(DBP)_2$ solids into a solution of uranium and nitric acid. The solutions were then stored for a sufficient length of time to allow the system to dissolve $UO_2(DBP)_2$ and come to equilibrium. Aliquots of each sample were withdrawn periodically to analyze to determine if the DBP concentration had equilibrated.

EXPERIMENTAL

Solutions were prepared with reagent grade HNO_3 and uranyl nitrate hexahydrate (UNH) and with 98% pure DBP solution obtained from Aldrich. Stock solutions of UNH and DBP were prepared in glass volumetric flasks with 0.5 M HNO_3 prepared from 15.7 M acid. For low-acid testing (0-0.5 M HNO_3), the UNH solution containing 630 mM U was prepared by dissolving 79.13 g of UNH solids in a 250 mL volumetric flask using 0.5 M HNO_3 and diluting to the mark. The HDBP solution was prepared by dissolving 0.2792 g of HDBP in a 100 mL glass volumetric flask using 0.5 M HNO_3 and diluting to the mark. The concentration of HDBP based on 98% purity is 13.09 mM. Duplicate analyses of the DBP stock solution gave an average concentration of 12.92 ± 0.05 mM. The stock solutions were then used to prepare test solutions.

For high-acid testing (0.1-4.0 M HNO_3), the UNH solution containing 630 mM U was prepared by dissolving 79.20 g of UNH solids in a 250 mL volumetric flask using 0.5 M HNO_3 and diluting to the mark. Two separate HDBP solutions were made. The first was made by dissolving 0.2804 g of HDBP in a 100 mL volumetric flask using 0.5 M HNO_3 and diluting to the mark. The nominal DBP concentration based on 98% purity is 13.16 mM. Four analyses of the HDBP stock solution gave an average concentration of 11.89 ± 0.38 mM. The second DBP solution was prepared by dissolving 0.8946 g of HDBP in a 200 mL glass volumetric flask using 0.4 M HNO_3 and diluting to the mark. The nominal concentration of HDBP based on 98% purity is 20.96 mM. The HDBP concentration was not verified analytically because its accuracy had little or no bearing on the results of the experiment for which it was used.

Low-Acid Precipitation Tests

Precipitation tests were done at ambient temperature (22-23°C) and at 0°C. Tests were carried out by preparing the solutions, and by allowing the solutions to sit in a hood at ambient temperature or in a constant temperature bath at 0°C. The

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samples were examined daily to see if precipitation had occurred. If precipitation of solids occurred during the test, samples were taken to analyze the DBP concentration remaining in solution. The quantity of solids precipitated was small enough that the concentrations of U and acid would not be significantly affected. The intent of the test is to add enough DBP to be near or above the solubility limit. However, if the components are near the solubility limit, super-saturation can occur, which results in slow solids formation.

Solutions were prepared for the first test at 0°C. Samples contained either 0.1 M or 0.5 M HNO_3 and either 25 mM or 50 mM uranium. The concentrations of DBP ranged between 0.52 and 1.70 mM. All samples eventually exhibited precipitation, so a second experiment at 0°C was performed with reduced DBP concentrations. The second test duplicated the first except that DBP concentrations were lowered to 0.19-0.62 mM.

The solutions were prepared in glass vials with Teflon liners in the caps to prevent adsorption of DBP by the plastic. The total solution volume in the vials was 25 mL in all cases. The samples were placed in the constant temperature bath at 0°C for several days before sampling and analysis. Two blanks were included as checks on the analyses.

Ambient temperature precipitation experiments at low HNO_3 concentrations were also performed. Starting solutions were prepared and stored until precipitation occurred. Samples were observed over a 60-day period. When precipitation occurred, a liquid sample was withdrawn and submitted for DBP analysis. Samples were prepared as follows: 1) 0.1 M HNO_3 and 0.52 mM DBP at 25, 50, 76, and 378 mM U; 2) 0.3 M HNO_3 and 1.70 mM DBP at 25, 50, 76, and 378 mM U; and 3) 0.5 M HNO_3 and 2.62 mM DBP at 25, 50, 76, and 378 mM U.

Low-Acid Dissolution of Solids

Solid $UO_2(DBP)_2$ was prepared by dissolving 9.97 g of UNH in 50 mL of deionized (DI) water and adding DBP prepared by washing 30 mL of a 50-50 mixture of DBP/MBP (monobutyl phosphate) three times with 10 mL portions of DI water. The MBP is highly water-soluble compared to DBP and should be removed by the water washes. Yellow solids separated immediately upon addition of DBP. The solids were sticky and were separated from the solution by filtration. The solids were dissolved in a small quantity of hot 2-ethylhexanol and re-precipitated by cooling with an ice bath.

The resulting solids were filtered and dried in air. Yellow powder was obtained after drying (9.5 g, 72 % yield). The x-ray pattern of the solids was similar to that of Pu DBP with no indication of more than one phase. Thermogravimetric

analysis of the solids further indicated the desired compound had been prepared.[8] These solids were then used in subsequent dissolution tests at 10°C and 30°C.

One half gram of solids were placed in glass vials with various amounts of UNH stock solution, the appropriate concentration of acid, and DI water to obtain the desired concentrations. In addition, vials were prepared with water and the three HNO_3 concentrations without any U present. The total volume, added to each vial was 25 mL. The vials were placed in a constant temperature bath at the desired temperature.

Periodic samples were taken for DBP analysis to determine if equilibrium had been reached. Equilibrium was assumed to be attained when the DBP analyses were within 1 % of the previous sample. When equilibrium was attained, samples were taken and analyzed for DBP, U, and free acid. The samples taken for analysis from the bath at 30°C were diluted with an equal volume of 0.5 M HNO_3 to ensure that precipitation did not occur when the samples cooled to ambient temperature. The test matrix contained samples with 0.1, 0.3, and 0.5 M nitric acid at 0, 25, 50, 76, and 378 mM uranium. Blank samples of DI water were submitted with all samples from this set. In addition, some solutions with known initial amounts of DBP in 25-76 mM U were prepared as standards and submitted along with the samples.

High-Acid Precipitation Tests

Precipitation tests were done at ambient temperature (22-23°C) and at 0°C. The samples had high DBP concentrations to cause rapid precipitation; the solutions precipitated within four hours and were allowed to equilibrate. Three sets of samples were made containing 0.1 M HNO_3/1.05 mM DBP, 0.5 M HNO_3/1.58 mM DBP, 1.0 M HNO_3/2.10 mM DBP, 2.0 M HNO_3/3.16 mM DBP, and 4.0 M HNO_3/6.32 mM DBP. The three sets included 1) 50 mM U at 0°C, 2) 50 mM U at 23°C, and 3) 25 mM U at 23°C.

The total solution volume in the vials was 12.5 mL in all cases. The samples were stored at the appropriate temperatures and sampled for DBP analyses after 4 days, 11 days, and 35 days to determine if equilibrium had been established. The quantity of solids precipitated was small enough that the concentrations of U and acid would not be significantly affected.

In a separate experiment, U-DBP solids were precipitated from 50 mM uranium solutions to observe their crystalline structures using x-ray diffraction (XRD). Nitric acid and DBP were as follows: 0.13 M HNO_3/4.82 mM DBP, 1.0 M HNO_3/4.82 mM DBP, and 4.0 M HNO_3/8.77 mM DBP. Sample bottles containing 100 mL of sample were prepared. After 16 hours, the solids were filtered and submitted for XRD analysis.

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Analyses

Analysis for U in solution was done by the Chem Check instrument, which utilizes U phosphorescence. DBP analyses were done by ion chromatographic analysis (IC). Considerable effort was made to improve the DBP analysis method to obtain reproducible results with the lowest uncertainty. Samples without U or high nitrate ion can be run without significant pretreatment. However, U and high nitrate can interfere with the analysis.

Nitrate ion at high concentration binds with more ion exchange sites on the analytical column causing DBP^- to elute in the void volume. Uranium complexes DBP so strongly ($\beta_1 = 2 \times 10^4$) that a portion of the DBP is not present as an anion[4] in the eluant, causing the results to be low. Both effects were overcome by pretreatment involving extraction of HDBP from the aqueous samples with 2-ethylhexanol followed by back-extraction into 1 M NaOH. The back-extracted solution was then put through ion exchange cartridges to remove the sodium ion and protonate DBP^- to HDBP. Optimum instrumental analysis was achieved in a pH range between 0 and 3. A standard U solution was periodically spiked with a known quantity of DBP and run through the procedure to check data interference from U and NO_3^- effects.

RESULTS AND DISCUSSION

The solubility of UO_2^{2+} in HNO_3 solutions containing DBP is expected to be a function of acid, DBP^-, and U concentrations, as can be seen from the reaction governing precipitation at low acid and uranium concentrations (equation 1).

$$UO_2^{2+} + 2\,HDBP \leftrightarrow UO_2(DBP)_{2,\,solid} + 2\,H^+ \quad (1)$$

A second precipitate can also form as nitric acid concentration, or possibly total nitrate, increases.[2]

$$UO_2^{2+} + 2\,HDBP + HNO_3 \leftrightarrow UO_2(NO_3)(H[DBP]_2)_{\,solid} + 2\,H^+ \quad (2)$$

Krutikov also reported that the two solids could be interchanged by varying the HNO_3 concentration, but did not test HNO_3 concentrations between 0.2 M and 6 M.[2]

$$UO_2(DBP)_{2,\,solid} + HNO_3 \leftrightarrow UO_2(NO_3)(H[DBP]_2)_{\,solid} \quad (3)$$

Temperature is also a variable since solubility generally increases with increasing temperature. The reactions given above are the overall reactions to yield

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a precipitate. There are actually several reactions and associated equilibrium constants involved as shown in equations 4-10 where the brackets in the equilibrium constants are for activity.[1]

$$HDBP \leftrightarrow H^+ + DBP^- \qquad K_a = [H^+][DBP^-]/[HDBP] \qquad (4)$$

$$2\ HDBP \leftrightarrow (HDBP)_2 \qquad K_{Dimer} = [(HDBP)_2]/[HDBP]^2 \qquad (5)$$

$$UO_2^{2+} + DBP^- \leftrightarrow UO_2(DBP)^{1+} \qquad \beta_1 = [UO_2(DBP)^{1+}]/[UO_2^{2+}][DBP^-] \qquad (6)$$

$$UO_2(DBP)^{1+} + DBP^- \leftrightarrow UO_2(DBP)_{2,\ sol'n} \qquad \beta_2 = [UO_2(DBP)_2]/[UO_2(DBP)^{1+}][DBP^-] \qquad (7)$$

$$UO_2^{2+} + 4\ DBP^- \leftrightarrow UO_2(DBP)_4^{2-} \qquad \beta_4 = [UO_2(DBP)_4^{2-}]/[UO_2^{2+}][DBP^-]^4 \qquad (8)$$

$$UO_2(DBP)_{2\ solid} \leftrightarrow UO_2^{2+} + 2\ DBP^- \qquad K_{sp} = [UO_2^{2+}][DBP^-]^2 \qquad (9)$$

The stability constant β_1 for the uranyl DBP complex is reported to be 2.0 x 10^4, and β_4 is reported at 2.5 x 10^8, but no value has been reported for β_2.[4] Two values have been reported for K_{sp} in the literature:[2,4] 6.1 x 10^{-11} and 7 x 10^{-12}. The first value was determined in 0.2 M HNO_3 solution. The latter value is an apparent K_{sp} rather than the thermodynamic K_{sp}, but conditions are not given.[4] A further complication is that two values are also reported for the acid dissociation constant (K_a) for HDBP, which differ by a factor of greater than five.[9,10] Krutikov used the higher value for K_a to calculate his K_{sp}.[2] Dibutyl phosphoric acid also forms a dimer in solution with a dimerization constant of 13.[9] Attempts to calculate the concentration of DBP^- at different acid and U concentrations using a value of 6.1x10^{-11} for the K_{sp} and a value of 0.1 for K_a did not give results which match the experimental data from this study.

The effect of the equilibria in equations 4, 5 and 9 on the concentration of DBP^- available for precipitation is shown in Figure 1. The dominant species will be DBP^- at low HNO_3 concentrations and HDBP at higher HNO_3 concentrations. The presence of the dimer [$(HDBP)_2$] is minor up to 4 M HNO_3 when the total DBP concentration is $<$ 0.004 M. These calculations were made with a U concentration of 25 mM. The activity coefficients for all DBP species were assumed to be 1 because the total concentration of DBP in solution is low especially at low HNO_3 concentration. However, the activity coefficients are not 1 for acid and U at these concentrations. Single ion activity coefficients were calculated for H^+ and UO_2^{2+} according to the method of Kielland and assuming that the effective diameter of the hydrated uranyl ion is the same as that given for Th^{4+}.[11] The calculation uses the ionic strength of the solutions, which is known to change activity coefficients of ions in solution.[12,13]

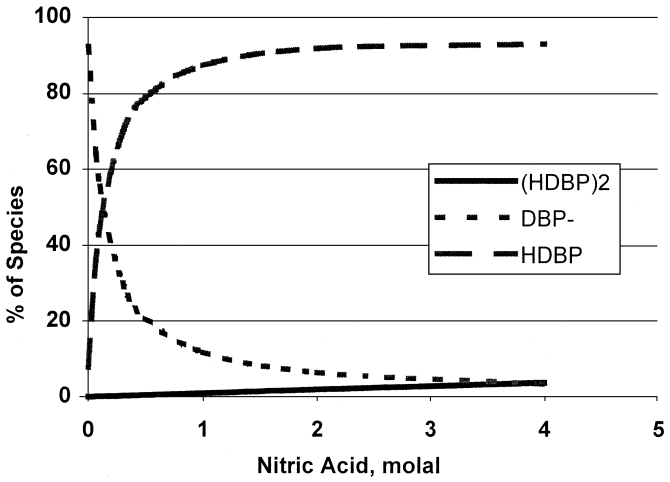

Figure 1. Calculated DBP speciation as a function of HNO_3 concentration.

U-DBP Solubility in Low Acid

The results from tests at 0°C and 23°C are shown in Tables 1 and 2. The results from the 0°C tests show that, within the analytical uncertainties, there is no difference in the DBP concentrations with 25 or 50 mM U at 0.1 M HNO_3. The final DBP concentration is statistically the same regardless of the starting DBP concentration. Reif noted that within his experimental conditions there was no detectable difference in precipitation behavior for 12 or 25 mM U solutions with 0.1 M HNO_3.[5] The concentration of DBP which can result in precipitation then is about 0.33 mM for both 25 and 50 mM U solutions at 0°C. It is uncertain whether the data at 0.5 M HNO_3 is different for 25 and 50 mM U. The 25 mM data have an average of 0.46 mM with a standard deviation of 0.017 mM. The 50 mM data have an average of 0.41 mM with a standard deviation of 0.010 mM. There is no difference in the numbers at two standard deviations. This result is not expected from solubility product considerations and is not explainable on a simple thermodynamic basis.

Tables 1 and 2 also show that super-saturation occurs in the solutions such that actual formation of solids can be delayed for as much as several months even though the DBP concentration exceeds the solubility limit. For example, some of the 0°C samples had been in the constant temperature bath for more than four weeks with solids forming in only two of the five samples that were expected to precipitate. The samples that precipitated took 7 to 8 days before solids appeared even though the apparent solubility limit was exceeded by 34% and 50%, respectively. Samples at 0.5 M HNO_3 and 0.53 mM U initially have 13% and 27% excess DBP,

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Table 1. Results for 0°C Solubility Tests

Calculated Starting Concentrations			Final Liquid Analysis	Calculated Starting Concentrations			Final Liquid Analysis
HNO3, M	U, mM	DBP, mM	DBP, mM	HNO3, M	U, mM	DBP, mM	DBP, mM
0.1	0	0.52	0.52	0.5	0	0.92	0.96
0.1	25	0.19	No ppt.	0.5	25	0.43	No ppt.
0.1	25	0.26	No ppt.	0.5	25	0.53	No ppt.
0.1	25	0.33	No ppt.	0.5	25	0.62	0.45 (7 days)
0.1	25	0.52	0.33	0.5	25	1.18	0.47
0.1	25	0.72	0.34	0.5	25	1.44	0.47
0.1	25	0.92	0.32	0.5	25	1.70	0.44
0.1	50	0.29	No ppt.	0.5	50	0.43	No ppt.
0.1	50	0.38	No ppt.	0.5	50	0.53	No ppt.
0.1	50	0.48	No ppt.	0.5	50	0.62	0.41 (8 days)
0.1	50	0.78	0.35	0.5	50	1.18	0.40
0.1	50	1.05	0.33	0.5	50	1.44	0.42
0.1	50	1.31	0.34	0.5	50	1.70	0.42

when compared against the DBP levels of those that precipitated, but did not precipitate. These data confirm that conditions of super-saturation can be established. The long times required to initiate precipitation, especially at the lower nitric acid concentrations, may be attributable to the high values for the β_1 and β_4 coefficients.

Table 2. Results for Ambient Temperature Solubility Tests

Calculated Concentrations			
HNO3, M	U, mM	DBP, mM	Time to Precipitate
0.1	25	0.52	No ppt. > 60 days
0.1	50	0.52	56 days
0.1	76	0.52	56 days
0.1	378	0.52	35 days
0.3	25	1.57	Immediate
0.3	50	1.57	Immediate
0.3	76	1.57	Immediate
0.3	378	1.57	16 days
0.5	25	2.62	Immediate
0.5	50	2.62	Immediate
0.5	76	2.62	Immediate
0.5	378	2.62	8 hours

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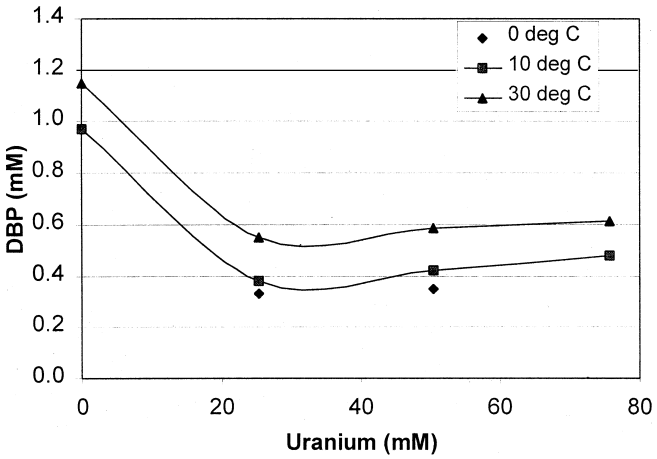

Figure 2. DBP solubility in uranium at 0.1M HNO_3.

The analytical data for DBP in the solutions at 23°C were not reliable having been analyzed prior to recent improvements in the analytical method; they are not reported. Observations about the time necessary for precipitation to occur are valid. Figures 2-5 and Table 3 summarize the remaining data for different temperatures at low HNO_3 concentrations. The data for 378 mM U is

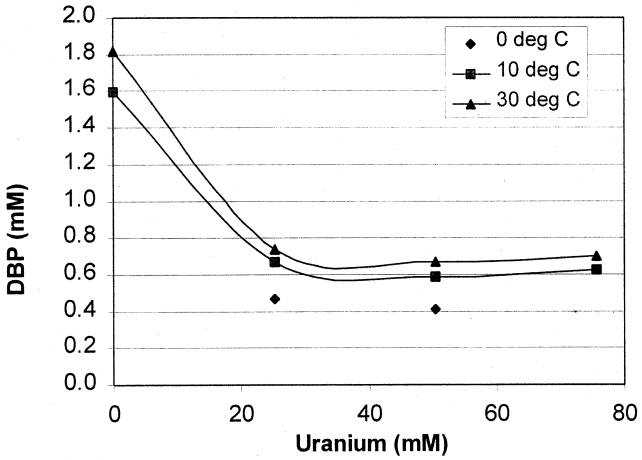

Figure 3. DBP solubility in uranium at 0.5M HNO_3.

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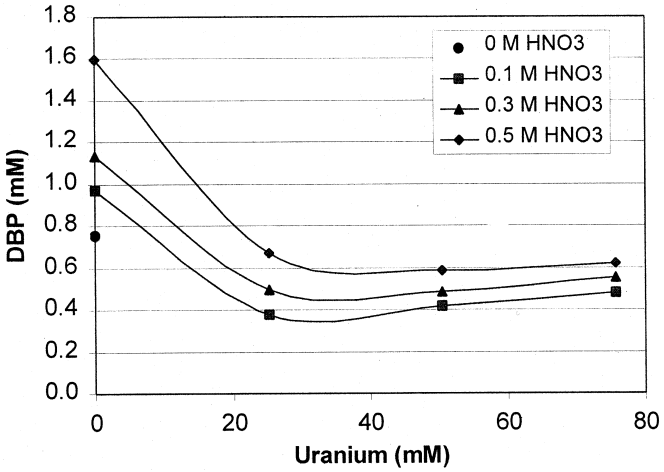

Figure 4. DBP solubility in uranium at 10°C.

not shown in the figures to provide clarity. The DBP concentrations required for precipitation at 378 mM U are slightly higher than for the lower concentrations shown in the figures. This phenomenon is due either to the increased ionic strength or to the formation of the charged complex ion shown in equation 6 above. The ionic strength will change the activity coefficients affecting

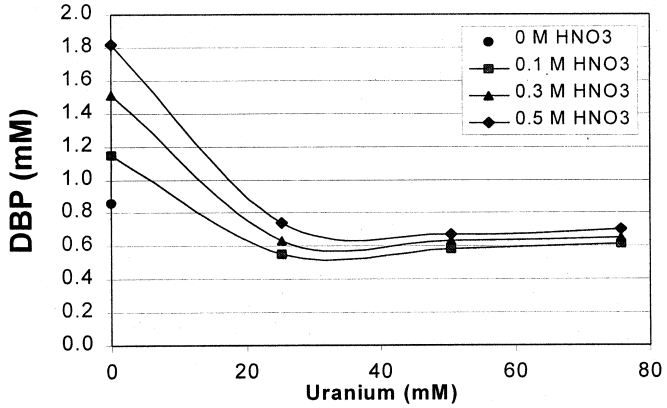

Figure 5. DBP solubility in uranium at 30°C.

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Table 3. Results of $UO_2(DBP)_2$ Solids Precipitation in Low Acid

	DBP Solubility Concentrations (mM)				
	U = 0mM	U = 25mM	U = 50mM	U = 76mM	U = 378mM
0 deg. C					
0.1M HNO_3		0.33	0.35		
0.5M HNO_3		0.46	0.41		
10 deg. C					
0 M HNO_3	0.76				
0.1M HNO_3	0.97	0.38	0.42	0.48	0.53
0.3M HNO_3	1.13	0.50	0.48	0.55	0.66
0.5M HNO_3	1.60	0.67	0.59	0.62	0.96
30 deg. C					
0 M HNO_3	0.86				
0.1M HNO_3	1.15	0.55	0.58	0.61	0.85
0.3M HNO_3	1.51	0.63	0.63	0.65	0.68
0.5M HNO_3	1.82	0.73	0.67	0.70	0.89

the activities in the system. High U concentration increases the amount of DBP present in solution as the complex ion, $UO_2(DBP)^{1+}$ as shown in equation 6.

Figures 2 and 3 show there is little change in DBP concentration required for precipitation as the U concentration changes at a constant HNO_3 concentration except for samples with no initial U present. Figures 4 and 5 show that the shape of the curves change slightly at higher acidity such that the apparent minimum concentration of DBP occurs at 50 mM in 0.5 M HNO_3 instead of 25 mM in 0.1 M HNO_3. In the range of nitric acid concentration tested, increasing the acid concentration by a factor of 5 from 0.1M to 0.5 M increases the DBP concentration required for precipitation by a maximum factor of two. That much increase is only observed at the lowest concentration. The increase is less at 50 and 76 mM U. Temperature appears to have the largest effect at low acidity, but the effect is reduced at higher acidity.

U-DBP Solubility in High Acid

The literature also discusses the finding of different uranium compounds at low HNO_3 concentrations when compared to those forming at higher acid concentrations. The literature indicates that at 0.2M HNO_3, $UO_2(DBP)_2$ is formed upon precipitation. However, in 6 M HNO_3 the precipitate is reported to be $UO_2(NO_3)(H[DBP]_2)$, $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$, or their mixture.[2,6]

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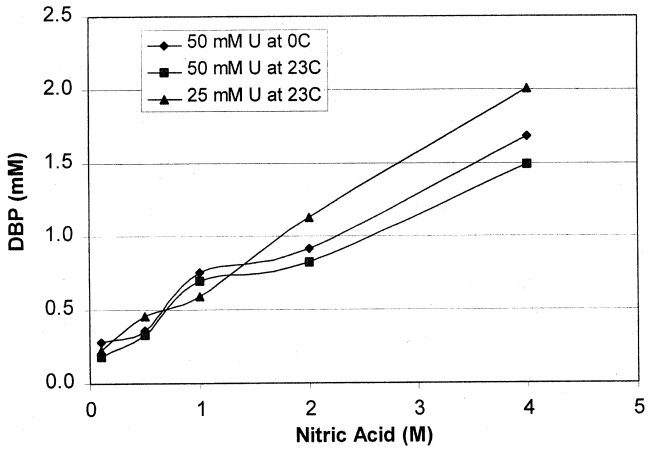

Figure 6. DBP solubility in uranium at high HNO_3 concentrations.

In light of Equations 1 and 2, it is not difficult to understand why NO_3^- becomes involved in the precipitation reaction when NO_3^- is a major component in solution (from nitric acid and uranyl nitrate). The literature does not present data or theory regarding compounds that exist between 0.2 and 6.0 M HNO_3. The same references also discuss inter-conversion between the various compounds meaning that the high acid compound, if placed in 0.2 M acid, will convert to $UO_2(DBP)_2$, and vice versa as shown in equation 3.

The final analyses for high acid solubility of U-DBP compounds are shown in Figure 6 and Table 4. An examination of the associated data shows that the data at 0°C for 0.1 M and 0.5 M HNO_3 is comparable to those from the low-acid solubility tests. Some concerns exist regarding the accuracy of the data at room tem-

Table 4. Results of $UO_2(DBP)_2$ Solids Precipitation in High Acid

	DBP Solubility Concentrations (mM)		
	25 mM U at 23 deg C	50 mM U at 23 deg C	50 mM U at 0 deg C
0.1M HNO3	0.22	0.19	0.28
0.5M HNO3	0.46	0.34	0.36
1.0M HNO3	0.59	0.70	0.76
2.0M HNO3	1.13	0.82	0.92
4.0M HNO3	2.00	1.49	1.68

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perature because, unlike the 0°C samples, the room temperature samples were stored in the light. Photolysis of TBP is a known occurrence, and it is unclear whether there is a photolysis of DBP occurring in these samples.[14] This is emphasized by the fact that the room temperature curve for 50 mM U is consistently below the curve for the samples at 0°C; U-DBP solubility should be higher at elevated temperatures.

Also, the data as a function of time show that DBP for low acid samples (0.1-0.5 M) starts at the levels reported earlier and then decreases with the analyses showing changes on the order of 20-35%. In contrast, the high acid data (2.0-4.0 M) remain essentially constant for duplicate and triplicate analyses with data variability on the order of 2-8%. This could be caused by slower kinetics in reaching equilibrium under low acid conditions or by the filtering of light in higher HNO_3 concentrations to prevent DBP degradation. More research needs to be performed to better understand and quantify the behavior of the system because it is possible that we have created a different system by intentionally spiking significant excesses of DBP into the system.

While the low acid data have an element of uncertainty, the high acid data show a good degree of repeatability as a function of time. Furthermore, an examination of Figure 6 shows a clear shift in DBP solubility between 0.5 M and 1.0 M HNO_3 for 50 mM U samples and between 1.0 M and 2.0 M HNO_3 for 25 mM U samples. Additional analysis of the slopes of the lines before and after the shifts reveals that the slopes for the three lines before the shift are essentially the same; this is also observed for the lines following the shift. The fact that the slopes of these lines are essentially the same implies that the same general reactions and equilibria are occurring in the three sets of samples.

The data is shown in Table 5 for both 10 and 30°C. An examination of the data shows that the ratio of DBP to U decreases as the nitric acid concentration increases. When no acid was present initially, the ratio is >2. At 0.5 M acid, the ratio is about 1. It is likely that U hydrolysis occurred after solids dissolution resulting in reprecipitation of some of the U as the hydroxide, which also would lead to the high acid analyses observed.

Table 5. Results of $UO_2(DBP)_2$ Solids Dissolution in Nitric Acid

Solution Analyses – 10°C				Solution Analyses – 30°C			
HNO3, M	U, mM	DBP, mM	DBP/U	HNO3, M	U, mM	DBP, mM	DBP/U
0.011	0.18	0.76	4.22	0.01	0.22	0.86	3.91
0.086	0.42	0.98	2.33	0.08	0.73	0.96	1.32
0.25	0.71	1.34	1.89	0.29	1.34	1.51	1.13
0.42	1.93	1.82	0.94	0.47	—	1.91	—

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The presence of the solubility shift is extremely interesting in light of the information in the literature regarding distinctly different compounds present at low acid (0.2 M) versus high acid (6 M).[2] XRD analysis of the solids from 0.2 M HNO_3 shows a close match to the crystalline pattern for $UO_2(DBP)_2$. Analyses of the compounds precipitated in 1.0 M HNO_3 clearly indicate that some molecular substitutions have occurred. XRD of the solids from 6.0 M HNO_3 shows a decreasing presence of $UO_2(DBP)_2$ and an increase in amorphous content. The XRD patterns for 0.2 and 6.0 M HNO_3 are shown in Figure 7. The increasing amorphous character of the solids from 6 M HNO_3 is consistent with Krutikov and Solovkin who described the solids created in 6 M HNO_3 as "viscous liquids" which form vitreous masses when washed with water in air.[2]

In combining XRD data with DBP solubility data, the increased DBP solubility during the solubility shift toward higher HNO_3 suggests the presence in significant quantities of compounds in equilibrium with $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$ because $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$ contains four DBP molecules per UO_2 molecule versus the two DBP molecules associated with $UO_2(NO_3)(H[DBP]_2)$. However, with only limited data available, it is difficult to draw firm conclusions about the nature of the compounds present during the DBP solubility shift.

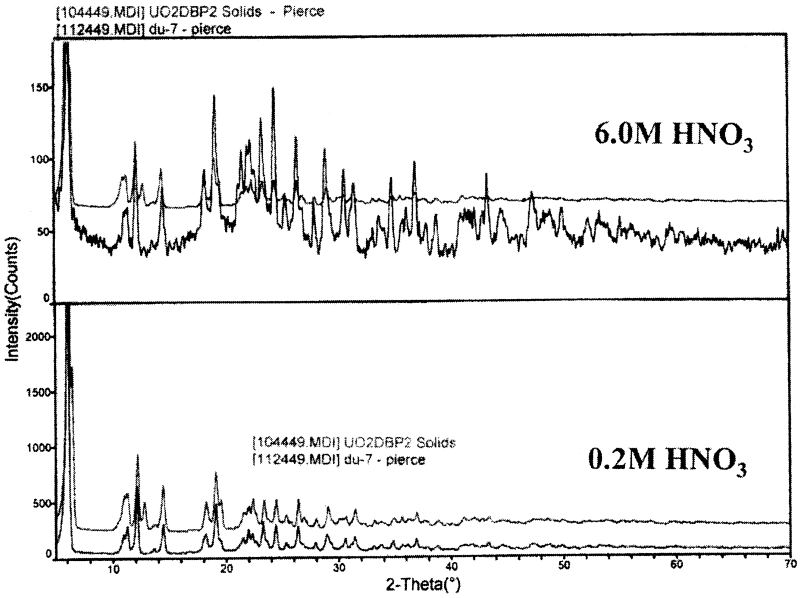

Figure 7. XRD patterns for compounds at low and high acid concentrations.

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CONCLUSIONS

Research has identified the solubility limits of nitric acid solutions containing both uranium and DBP. Dibutylphosphate solubility limits have been experimentally determined over the range of 0-0.5 M HNO_3, 0-76 mM U, and 0-30°C. The solubility of $UO_2(DBP)_2$ in nitric acid passes through a minimum at 29-38 mM U. The presence of a minimum reflects the change in ionic strength of the solution as uranyl nitrate is added.

Evaluation of solubility behavior from 0-4.0 M HNO_3 appears to confirm the work of Krutikov and Solovkin[2] in reporting low- and high-acid compounds containing two DBP^- ions per UO_2^{2+} ion. The data from XRD demonstrate that the compounds at low and high HNO_3 concentrations are different. The high-acid data also revealed a DBP solubility shift between 0.5 M and 1.0 M HNO_3 for 25-50 mM uranium. The shift may be attributed to different compounds present during the transition from UO_2DBP_2 at low acid to $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$ at high acid.

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