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Review of Physical and Chemical Properties of Tributyl Phosphate/Diluent/Nitric Acid Systems

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Numerous publications have examined the chemical and physical aspects of tributyl phosphate (TBP), TBP/nitric acid, and TBP/diluent/nitric acid systems, but there are some discrepancies within the available data. There is also a lack of data on the physical properties of TBP at temperatures above 60°C. A review of more than 100 references, covering the physical and chemical properties of TBP and related systems will be presented. Data on solvent degradation and kinetics of the interactions occurring in these systems will be provided and compared. Also the existing data on TBP vapor pressure, solubility, and density will be discussed.

Keywords density; solubility; solvent extraction; TBP; vapor pressure

INTRODUCTION

Reprocessing of used nuclear fuels began during the World War II period to obtain weapons materials. During this time period, several methods for extracting plutonium from the irradiated uranium were studied, among them, bismuth phosphate which was abandoned because of high waste volumes and relatively low recovery. Though several methods of extraction were actively studied, solvent extraction, in particular the PUREX process with tri-n-butyl-phosphate (TBP) as the solvent, forged ahead and now dominates the reprocessing industry to separate specifically U(VI) and Pu(IV). TBP has the advantages of being more stable, less flammable and results in better separation than other solvents. Even though numerous publications have examined the chemical and physical aspects of TBP over the years, there are still discrepancies or lack of data on TBP/diluent/nitric acid chemistry, especially at elevated temperatures.

In this work, a literature review covering the physical and chemical properties of TBP, TBP/nitric acid, and TBP/diluent/nitric acid systems will be presented. A majority of the previous work has focused on TBP solvent degradation and the kinetics of TBP/nitric acid interactions. In order to understand the chemistry in the TBP/HNO_3 system, it is also necessary to know certain physical properties. This review will include the vapor pressure, solubility, and density of TBP and its main degradation product, dibutyl phosphoric acid (HDBP). The variables investigated will include HNO_3 concentration, temperature, and the presence of alkane diluent and metal nitrates.

SOLVENT DEGRADATION

TBP Degradation Products

There have been many investigations into the degradation of TBP under different types of systems and conditions. The two most important types of reactions studied are hydrolysis and radiolysis of the solvent and the degradation products, but other known reactions include oxidation, nitrolysis, and pyrolysis (1–21). In 1995 Tahraoui published a literature review of the decomposition of solvent extraction media during nuclear reprocessing which focused on the mechanisms for chemical and radiolytic degradation of TBP and diluents (22). Decomposition reactions of TBP are presented in Fig. 1 and Table 1 lists the pertinent chemical formulas and abbreviations. The principal degradation reaction is the hydrolysis of TBP to form HDBP and butanol. HDBP can undergo further hydrolysis, and butanol can undergo nitrolysis (producing butyl nitrate) or oxidation (producing carboxylic acids). All of the degradation products can undergo thermal pyrolysis leading to the gases labeled as end-products in Fig. 1.

A large majority of the work performed on the degradation of TBP and TBP/diluent systems has focused on radiolytic TBP decomposition and the effects on solvent extraction processes (4,10,11,14,16,23–29). Studies have included radiolysis and hydrolysis of TBP (4,11,14,15, 26,27) as well as TBP/diluent systems (10,13,16,23,25, 27–29). Most of the work was done on the organic phase alone, but there are also degradation studies on two-phase systems with and without the presence of heavy metals (U and Pu) (4,11,23). The degradation has been investigated as a function of [HNO_3], [TBP], [HDBP], [H_2MBP], temperature, diluent, and dose (13,25,28). The major and minor products have been identified by gas chromatography (GC),

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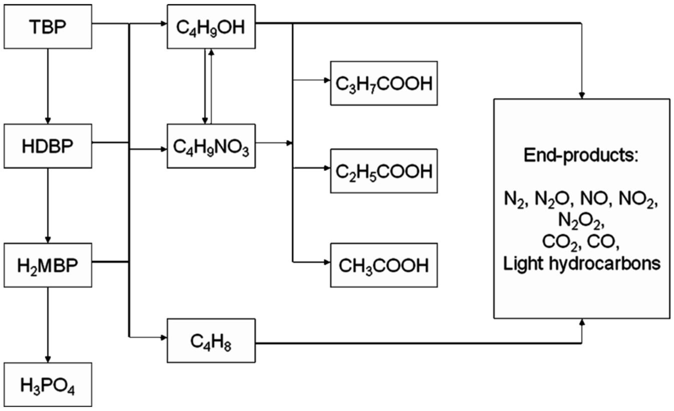

FIG. 1. Simplified reaction scheme of TBP degradation in contact with nitric acid in nitrate aqueous solutions.

infrared spectroscopy (IR), and thin layer chromatography (TLC) (13,27,29). The kinetics and mechanisms for degradation of TBP have been determined from these studies (16,26,29).

It is important to understand the composition of the gases formed by TBP degradation and their flammability so there have been several studies to determine this, but the results are not consistent. For example, it has been reported that the major flammable decomposition product is butene (1,21,30), and that after 8 hours at 220°C it makes up over 99% of the total gas formed (31). While another study reports that gas collected after TBP interactions with HNO_3 at 250°C contained little to no butene (32). It has also been shown that butyl nitrate is the major volatile product and causes explosion concerns (30,33,34), but one thermal degradation experiment found that butyl nitrate is not a major product as it rapidly decomposes upon production (1). A third flammable product, butyric acid, was reported in one study (30). Organic gas products of TBP hydrolysis/nitrolysis were subjected to further degradation by boiling in 20 M HNO_3 to form the final products of CO_2 and short-chain aliphatic acids, like formic acid (35). There is more agreement concerning the inorganic gases produced being N_2, CO, NO, CO_2, and N_2O, although there is no consensus on the concentrations formed (21,30,36,37).

TABLE 1
Chemical nomenclature of the species

Name	Abbrev.	Formula
Tri-n-butyl phosphate	TBP	$(C_4H_9O)_3PO$
Dibutyl phosphate	HDBP	$(C_4H_9O)_2PO(OH)$
Monobutyl phosphate	H_2MBP	$(C_4H_9O)PO(OH)_2$
Butyl alcohol or Butanol	BuOH	C_4H_9OH
Butyl nitrate	$BuNO_3$	$C_4H_9NO_3$
Phosphoric acid		H_3PO_4
Butene		C_4H_8
Butyric Acid		C_3H_7COOH
Propionic Acid		C_2H_5COOH
Acetic Acid		CH_3COOH

The decomposition of TBP and TBP/diluent system leads to liquid products as well as gases, and there have been several investigations in order to determine the identity of these products. It is well known that the major degradation product is HDBP (9,36–44). HDBP hydrolyzes in the presence of HNO_3 to form H_2MBP and finally H_3PO_4 (45), and therefore, both have been reported as degradation products of TBP (38,39,41,43,44). HDBP and H_2MBP are of particular concern due to their being strong complexants. Studies have found that they each form large polymers as well as complexes with several metal ions, including those of Pu, U, and Zr (33,38,39,46).

Butyl nitrate has been found as a liquid product, as well as being in the gas phase, and a few reports name it as a major product along with HDBP and water (36,37,43). Along with butyl nitrate, the other nonphosphate products are mainly butanol and only slight amounts of carboxylic acids (2,41,43). One study actually found that the amount of nonphosphate degradation products is equal to the amount of phosphate degradation products (2). The liquid products can either stay in the organic solvent phase or transfer into the aqueous nitric acid phase. Some work has been done to determine where the major products end up. The HDBP is soluble in the organic phase and it has been shown that over 90% of the HDBP formed stays in the solvent (7,42,47,48). The amount of H_2MBP formed is generally very small which makes it difficult to measure, but it has been determined that it is miscible in the aqueous phase (7,48). It can form organic complexes with association of HDBP or TBP leading to a slight retention in the organic phase of about 25% (48). The butanol moves into the aqueous phase, while butyl nitrate has actually been found in both the aqueous and organic phases as well as the gas (44,49).

Kinetics of TBP Degradation

There have been many studies on the kinetics of TBP solvent degradation. The variables of these investigations have been [HNO_3], [TBP], diluent, temperature, metal ion presence, and radiation dose (1,3,5,7,8,17–19,21,31,33,38, 41,42,50–60). The studies have compared single and two-phase systems, and even the decomposition of TBP dissolved in an aqueous phase (7,20,53,54,56,57). It was shown that TBP degradation increases with the temperature and the dose rate (8,17,19,41,54,56). It was also shown that degradation generally increased with [HNO_3], except under conditions of very high temperatures or radiation doses since the nitric acid effects are much less pronounced (7,17,41,55). One study found that the reaction rates were the same in one-phase and two-phase systems (54), but another experiment found the reaction rate is an order of magnitude less in a single organic phase than that in a two-phase system meaning that the HNO_3 from the aqueous phase is actively reacting with the organic phase (53). Hydrolysis of TBP dissolved in an aqueous phase is 30–40 times faster than in the organic phase (56).

Two common ways of determining TBP decomposition kinetics is measuring the gas evolution or HDBP formation over time. The use of these two different methods for describing reaction kinetics is most likely the reason there are so many discrepancies in the reported results. There have been several studies on the kinetics of gas evolution on a variety of systems and conditions (1,5,8,19,50,53,57). The kinetics of HDBP formation and accumulation has also been the focus of several studies (5,17,31,38,54). Formation rates of H_2MBP and H_3PO_4 are much lower than HDBP which increases slightly with $[HNO_3]$ (17). Temperature has a pronounced effect on TBP degradation rates. Thermal decomposition of TBP leads to conversion of 1.2% of initial TBP to HDBP after 70 hours at 178°C and to 8.4% conversion after just 2 hours at 240°C. This corresponds to reaction rate constants of $0.389 \times 10^{-7}\,s^{-1}$ for 178°C and $132 \times 10^{-7}\,s^{-1}$ for 240°C (31). Table 2 provides data on the formation rate of HDBP in an organic phase of 30% TBP contacted with varied aqueous phases and temperatures.

There have been many reports of TBP hydrolysis rate constants for both single and two-phase systems (3,7,18,20,33,38,52,56,58–61). Equation (1) exhibits a general reaction scheme for the hydrolysis of TBP with rate constants k_1, k_2, and k_3. Most studies agree that the reaction is first order with respect to $[HNO_3]$ (7,52,56,58), but one study concluded that between 1.5 M to 3 M HNO_3 the reaction rate is independent of $[HNO_3]$ (60). TBP hydrolyzes slowly in contact with 3 M HNO_3 at rates of 0.045%/day and 0.23%/day at temperatures of 76°C and 105°C, respectively. HDBP and H_2MBP exhibit pseudo-first-order hydrolysis rates in contact with 3 M HNO_3 at 76°C with half lives of 8 and 18 days. As a comparison at 25°C, H_2MBP in 3 M HNO_3 had a half life of 300 days (58). One study suggested that the HDBP hydrolysis rate constant could be approximated as 2/3 of that of TBP (52). Review of literature data found k_1 to be scattered and data for k_2 and k_3 almost completely lacking (56). Tables 3 through 7 summarize most of the reports of the hydrolysis constants of TBP. It can be concluded that the hydrolysis rate increases with temperature and slightly increases with $[HNO_3]$, and that the hydrolysis rate of TBP dissolved in the aqueous phase is about one order of magnitude higher than when hydrolysis occurs in the organic phase.

TABLE 3
Hydrolysis rate constant, k_1 (hr^{-1}), in organic phase of a two phase 30% TBP/diluent system*

Temp (°C)	H_2O	1.5–3 M HNO_3	3 M HNO_3
23.5	—	—	2.99×10^{-7}
25	7.2×10^{-8}	8×10^{-8}	—
40	—	9×10^{-7}	—
50	—	—	1.01×10^{-5}
60	—	3×10^{-5}	—
75	—	—	1.41×10^{-4}
80	—	2.6×10^{-4}	—
95	—	1.5×10^{-2}	—
Ref.	(3)	(60)	(56)

*—Implies no data reported.

TBP hydrolysis reactions:

$$TBP \xrightarrow{k_1} HDBP \xrightarrow{k_2} H_2MBP \xrightarrow{k_3} H_3PO_4$$

Diluent Degradation

The addition of a diluent improves physical properties of TBP which is necessary for large scale solvent extraction processes. The benefit comes about by decreasing viscosity and density of the organic solvent phase which in turn improves the phase separation and decreases criticality concerns (41,62–64). Many diluents have been investigated for their radiation and chemical behavior under conditions found to be similar to those in reprocessing. During these studies of the radiation chemistry of TBP in diluents, it

TABLE 2
HDBP formation rate (mg HDBP/L·h) in two-phase 30% TBP/dodecane system*

$[HNO_3]$ (aq)	25°C	50°C	75°C	80°C	Ref.
0.5 M	0.019	0.38	5.3	—	(38)
3 M	0.085	2.3	31.7	—	(38)
3.5 M	0.2	3.5	—	75	(54)

*—Implies no data reported.

TABLE 4
Hydrolysis rate constant, k_2 (hr^{-1}), in organic phase of a two phase 30% TBP/diluent system (60)

Temperature (°C)	1.5–3 M HNO_3
25	2×10^{-5}
40	8×10^{-5}
60	5×10^{-4}
80	2×10^{-3}
95	1×10^{-2}

TABLE 5
Hydrolysis rate constant, k_1 (hr^{-1}), of TBP dissolved in the aqueous phase*

[HNO_3]	50°C	75°C	90°C	Ref.
0.5 M	1.18×10^{-4}	1.86×10^{-3}	8.12×10^{-3}	(38)
1 M	2.1×10^{-4}	—	—	(20)
3 M	2.96×10^{-4}	6.35×10^{-3}	2.31×10^{-2}	(38)
5 M	5.0×10^{-4}	—	—	(20)
6 M	1.14×10^{-3}	8.7×10^{-3}	4.26×10^{-2}	(38)

*—Implies no data reported.

TABLE 6
Hydrolysis rate constant, k_2 (hr^{-1}), of TBP dissolved in the aqueous phase*

[HNO_3]	50°C	75°C	90°C	Ref.
0.5 M	2.48×10^{-5}	4.94×10^{-4}	2.44×10^{-3}	(38)
3 M	1.24×10^{-4}	2.33×10^{-3}	1.03×10^{-2}	(38)
5 M	—	3.5×10^{-3}	—	(20)
6 M	4.57×10^{-4}	4.6×10^{-3}	1.88×10^{-2}	(38)

*—Implies no data reported.

TABLE 7
Hydrolysis rate constant, k_3 (hr^{-1}), of TBP dissolved in the aqueous phase (38)

[HNO_3]	50°C	75°C	90°C
0.5 M	1.67×10^{-5}	2.65×10^{-4}	1.15×10^{-3}
3 M	6.21×10^{-5}	1.01×10^{-3}	3.8×10^{-3}
6 M	1.22×10^{-4}	2.3×10^{-3}	4.6×10^{-3}

was generally found that hydrocarbons (also called paraffins) had lower radiolysis yields than other functionalized solvents (18,65). Diluent nitration causes reduction in heavy metal- fission product decontamination factors in the extraction process. It has been shown that nitration of unsaturated hydrocarbon diluents in the presence of 3 M HNO_3 and 0.02 M HNO_2 occurs at 60°C, while for diluents composed of saturated hydrocarbons, nitration in 6 M HNO_3 did not occur until 105°C (51). Diluent type has an important role in solvent nitration and normal paraffin hydrocarbons are more resistant against nitration, and dodecane was found to be the most nitration resistant normal paraffin hydrocarbon (63). Another study of different types of hydrocarbon diluent interactions with HNO_3 found that reactivity increases as follow: normal paraffins < branched paraffins < cycloparaffins (41).

In industry, n-dodecane is the diluent used in Japan, but other diluents are used worldwide, namely hydrogenated propylene tetramer (HPT) in France and odorless kerosene in the UK. Dodecane is a commonly used diluent for laboratory experiments on the TBP-HNO_3 extraction system. This reagent is commercially available and can provide reproducible results based on its purity. Dodecane is also found to be chemically inert and highly radiation resistant (41,62). Due to the interest in dodecane as a diluent for TBP extraction processes, work has been done to understand its physical and chemical properties (52,66,67). One study showed that diluting TBP in dodecane demonstrated a decrease in the energetics of nitric acid interactions with TBP (32). Another study of thermal stability has shown that in an open, two-phase system at 100°C, the amount of gas evolution, which represents degradation, was the same for pure TBP and 30% TBP/dodecane with an 8 M HNO_3 aqueous phase, but under the same experimental conditions with an aqueous phase of 12 M HNO_3, the results showed the gas evolution rate for the 30% TBP/dodecane system to be approximately twice as high as that for 100% TBP (53).

Dodecane is relatively inert to chemical and radiolytic degradation, but of course there is a limit. An investigation into the stability of dodecane toward radiolysis found that an absorbed dose of less than 50 Wh/dm^3 had little to no effect on the density, viscosity, and phase separation time, but at higher doses each of the three properties were shown to increase exponentially due to the evolution of radiolytic degradation products (68).

There have been a few studies to determine the degradation products of hydrocarbon diluents, such as dodecane, and how they might interfere with the Purex process chemistry (69). The degradation products of normal paraffin hydrocarbon diluents include alkane nitro and nitrite compounds, alcohols, unsaturated alcohols, nitro alkenes, and carboxylic acids (41,70,71). There is also a report of small amounts of hydroxamic acids present in solutions of nitric acid degraded dodecane (72). Quantitative analysis of carboxylic acids formed by degradation of dodecane found the highest concentration formed to be 0.1 M in a system contacted with 14.5 M HNO_3 at 90°C for 7 hours (71). The degradation rate of hydrocarbons increases with increasing temperature and [HNO_3], and decreases with sparging due to removal of NO_2 (70). It has been shown that the nitrated paraffins will stay in the organic phase of the system until hydrolyzed to alcohol, which was found in low concentrations in the aqueous phase (41).

PHYSICAL PROPERTIES

Vapor Pressure

It was established that a transpiration method was the best technique for measuring TBP and water vapor pressure for single and two-phase systems, and this procedure and apparatus were described (73,74). There has been data collected for the vapor pressure of TBP, dodecane, HNO_3, and H_2O individually, and only one study tried to calculate the vapor pressure of a TBP/HNO_3 mixture (75).

There have been a number of reports of vapor pressure of liquid (pure) HNO_3 (76–80). Usually 70% HNO_3 is considered concentrated nitric acid, and this concentration has a vapor pressure of 6.46 mmHg at 20°C (77). A few studies have determined the partial pressure of HNO_3 over mixtures of the aqueous phase, and found that the vapor pressure of HNO_3 increases with [HNO_3] and temperature (75,81). Also it was shown that the vapor pressure of water is higher than that of nitric acid (75).

There is also a small amount of data on the vapor pressure of the organic phase. There have been a few reports of the vapor pressure of TBP at different temperatures (53,82,83), as there have been for dodecane (52,62). The vapor pressure of TBP at room temperature varies by nearly an order of magnitude likely due to the difficulty of determining a vapor pressure that is very low. There is no data on the vapor pressure of HDBP or of TBP/diluent/HNO_3 systems. Table 8 lists the data available on vapor pressure at different temperatures.

TABLE 8
Vapor pressure of pure organics at varied temperature*

Temp.	TBP	Source	Dodecane	Ref.
25°C	0.93 Pa	(18)	21 Pa	(62)
25°C	0.15 Pa	(82)	—	—
50°C	1.59 Pa	(82)	87 Pa	(62)
80°C	31.9 Pa	(82)	—	—
100°C	133.3 Pa	(52)	1866.5 Pa	(52)

*—Implies no data reported.

Solubility

The most common procedure for determining TBP solubility was using ^{32}P labeled TBP and measuring [TBP] in the aqueous phase by counting ^{32}P (84). There is much more data available on the solubility of this system than on the vapor pressure. The solubilities of water and HNO_3 in TBP and HDBP have also been reported (46,58,84–88). It was found that the solubility of water in TBP was 3.59 mol/L at 25°C and decreased with temperature (85,88). A mathematical model gave a maximum solubility of H_2O in TBP of 1.52 mol/L and a maximum solubility of 2.79 mol/L for HNO_3, each calculated assuming an organic phase with a mole fraction of TBP equal to 1 was in equilibrium with an aqueous phase containing 5.5 M HNO_3 (52). Solubility of water in HDBP was found to be relatively constant at 78 g/L from 25–60°C (58). Another report has a value of 1.2 g/mL at room temperature (46). Water and H_2MBP are completely miscible (46). The mutual solubility of water in dodecane is negligibly small (89,90).

TABLE 9
Solubility of TBP in aqueous nitric acid at 25°C*

[HNO_3]	100% TBP	30% TBP	Ref.
0 (H_2O)	0.45 g/L	0.3 g/L	(96,101)
2 M	0.3 g/L	0.3 g/L	(96)
3 M	0.2 g/L	—	(102)

*—Implies no data reported.

This section will mainly focus on the solubility of the organic phase in the aqueous phase, of which there have been several reports (3,21,30,42,51,58,75,84,85,89,91–100). Studies on TBP solubility in H_2O and HNO_3 show that solubility is low at room temperature, typically reported as between 200–300 mg/L, and decreases with diluent to TBP ratio (91,93). It has also been shown that TBP solubility decreases with [HNO_3] until 8–9 M, after which there is an increasing trend (93,101). Table 9 provides some data on the solubility of TBP and TBP/diluent in water and HNO_3 at room temperature and shows the effects of [HNO_3] to be more pronounced than the amount of diluent.

There are discrepancies in the literature on solubility data as a function of temperature. One study reports the solubility of TBP in the aqueous phase decreases with temperature (95), but three others declare that temperature increases the solubility of TBP (30,89,100). Studies of TBP solubility in aqueous solutions of uranyl or plutonium nitrate show that solubility decreases with metal ion concentration (21,89,91). Table 10 shows solubility data of TBP in aqueous solutions of concentrated $UO_2(NO_3)_2$ and data in 3 M HNO_3, and demonstrates the increase of

TABLE 10
Solubility data of TBP in aqueous phases at varied temperatures (g/L)*

Temp.	3 M HNO_3	0.7 M HNO_3/ 600 g/L $UO_2(NO_3)_2$	1200 g/L $UO_2(NO_3)_2$	Ref.
25°C	0.2	—	—	(20)
40°C	—	0.092	—	(100)
60°C	—	0.136	0.44	(100)
76°C	0.35	—	0.91	(20,100)
100°C	—	0.221	1.70	(100)
105°C	0.4	—	—	(20)
120°C	—	—	3.65	(100)

*—Implies no data reported.

solubility with temperature. Table 10 shows that the presence of a metal nitrate decreases the solubility of TBP, except at very high concentrations. There is actually very little to compare at elevated temperatures. A review of TBP/water solubility studies shows no reliable data above 60°C (85). A mathematical model was developed to describe the solubility of TBP in an aqueous phase of TBP/dodecane-HNO_3 biphasic system as function of $[HNO_3]$ and [TBP], but could not be applied as a function of temperature because of a lack of data (92).

There have been some solubility studies on the major TBP degradation products. Most work has been done on HDBP since it is found in much higher concentration (3,58,97–100), but some work has been focused on H_2MBP solubility (98). H_2MBP is completely miscible in H_2O and HNO_3 (98). It was also demonstrated that H_2MBP solubility is very low in kerosene, unless TBP or HDBP are present, then the solubility increases dramatically (98).

Although the solubility of HDBP in the aqueous phase is higher than TBP, most available data shows it follows similar trends with $[HNO_3]$ and temperature, and also includes similar discrepancies and missing data points. It was shown in one study that at constant temperature the solubility of HDBP in HNO_3 is relatively constant from $1-8$ M HNO_3 (98), but another study claims that the solubility increases in that same region (58). It has also been demonstrated that solubility of HDBP in HNO_3 increases with temperature (3,58,99,100), but the solubility in water decreases with temperature (58). Tables 11 and 12 show the trends with $[HNO_3]$ and temperature, but there are not very many data points, and the trends are not necessarily clear. This data does show that the variation is relatively small over a wide range of conditions.

A few studies have determined HDBP solubility in $HNO_3/UO_2(NO_3)_2$ solutions which is very important since HDBP is known to form complexes and even precipitates with U(VI) (97,99,100). The results of these studies show HDBP solubility to increase with $[HNO_3]$, and decrease with $[UO_2^{2+}]$ due to precipitation (97,99). HDBP solubility data obtained in nitric acid solutions containing low and high uranium concentration are shown in Tables 13 and 14, respectively. These tables demonstrate that the presence of uranyl nitrate in an aqueous phase of a given nitric acid concentration decreases the solubility of HDBP in that phase, but also for a given set of conditions, the addition of more uranyl nitrate can either increase or decrease the HDBP solubility. This data implies that the solubility of HDBP is very dependent on the chemical interactions between HDBP and $UO_2(NO_3)_2$. Table 14 also shows a clear dependence on temperature.

TABLE 11
Solubility of HDBP in aqueous phases

Aqueous	Solubility	Ref.
H_2O	0.082 mol/L	(3,98)
1–8 M HNO_3	0.035 mol/L	(98)
14 M HNO_3	0.08 mol/L	(98)

TABLE 12
Solubility of HDBP (g/L) in aqueous phases (58)*

Temp.	H_2O	1 M HNO_3	3 M HNO_3	4 M HNO_3
30°C	16	7	7	12
80°C	—	—	—	14
90°C	—	—	12	—
95°C	5	—	—	—
100°C	—	10	—	—

*—Implies no data reported.

TABLE 13
Solubility of HDBP (mM) in aqueous phases (99)*

Aqueous/temp.	23°C	30°C
H_2O	—	0.86
0.5 $MHNO_3$	—	1.82
0.5 M HNO_3/378 mM $UO_2(NO_3)_2$	—	0.89
1 M HNO_3/25 mM $UO_2(NO_3)_2$	0.59	—
1 M HNO_3/50 mM $UO_2(NO_3)_2$	0.7	—
4 M HNO_3/25 mM $UO_2(NO_3)_2$	2.0	—
4 M HNO_3/50 mM $UO_2(NO_3)_2$	1.49	—

*—Implies no data reported.

Density

The density of the aqueous and organic phases has been investigated as functions of concentration and temperature. These studies seem more complete and the results are more consistent than the data on vapor pressure or solubility. Studies on the aqueous phase show the density of HNO_3 and $HNO_3/UO_2(NO_3)_2$ solutions decrease with temperature and increase with $[HNO_3]$ and $[UO_2^{2+}]$

TABLE 14
Solubility of HDBP (g/L) in concentrated uranyl solution (100)*

Aqueous/temp.	40°C	60°C	100°C	120°C
0.7 M HNO_3/600 g/L $UO_2(NO_3)_2$	0.291	1.04	3.05	—
1200 g/L $UO_2(NO_3)_2$	—	7.5	13.0	14.8

*—Implies no data reported.

TABLE 15
Summary of density data (g/mL)*

Solution/temp.	20°C	Ref.	23°C	Ref.	25°C	Ref.	55°C	Ref.
Dodecane	0.748	(68,75)	—	—	0.7458	(103)	0.7238	(103)
TBP	0.967	(104)	0.976	(58)	0.971–0.973	(62,103)	0.9449	(103)
HDBP	1.116	(104)	1.065	(58)	—	—	—	—
H_2MBP	—	—	1.220	(58)	—	—	—	—
30%TBP/n-dodecane	—	—	0.810	(104)	0.7458	(103)	0.7237	(103)
30%TBP/dodecane contacted with 0.5 M HNO_3	—	—	0.813	(104)	—	—	—	—
30%TBP/dodecane contacted with 3 M HNO_3	—	—	0.837	(104)	—	—	—	—

*—Implies no data reported.

(21,75,87). The density of each of the organic components has been studied separately as a function of temperature, and shows a decreasing trend with increasing temperature (18,29,58,68,75,86,103). Densities of a variety of organic phase compositions have been determined. The combinations include TBP/HNO_3, TBP/dodecane, $TBP/UO_2(NO_3)_2$, $30\%TBP/dodecane/HNO_3$, $30\%TBP/dodecane/HNO_3/UO_2(NO_3)_2$, and single and two-phase systems (21,75,87,103,104). In general the results show a decrease in density as temperature increases, and an increase with $[HNO_3]$ and $[UO_2^{2+}]$ (21,103,104). From all of the available data a few mathematical models have been developed to predict the density of the organic phase under a wide variety of conditions (102,105,106). A summary of results from the most extensive density studies is found in Table 15, including the organic components and even a 30% TBP/dodecane phase before and after contacting with nitric acid. Some discrepancies are found where the density is not decreasing with temperature or decreasing by a relatively large amount over a small temperature variation. This table also demonstrates that there are still many missing data points, especially at elevated temperatures.

CONCLUSIONS

As this review has demonstrated, there has been a plethora of investigations into TBP-nitric acid chemistry. Although there is an enormous amount of reliable data on this system, this report only focused on a very limited area, and found several discrepancies and entire segments of missing data. In particular, there is no consensus on the gaseous degradation products of TBP, nor is there complete agreement on the kinetics of TBP degradation. Also there is data on the physical properties of TBP, TBP/nitric acid, and TBP/diluent/nitric acid systems, but the available data does not create a complete picture of the fundamental chemistry occurring during extraction processes with TBP. There is very limited amount of data on the vapor pressure of these organic systems. There is much more available data on the solubility of the organic solutions into the aqueous solutions and on the density of both phases, but some of the existing data is contradictory. Also it was found there is a lack of information on the physical properties of this system at temperatures above 60°C.

This literature review leads to questioning the reliability of some of the data presented within. Nearly all of the work cited seems to be trustworthy, but clearly all reports cannot be accurate since there are contradictions. This causes confusion concerning the chemistry of TBP-nitric acid interactions and which data is reliable. In order to elucidate the fundamental properties of TBP, TBP/nitric acid, and TBP/diluent/nitric acid systems, more experimental data needs to be obtained. Currently, UNLV is planning experiments to confirm and/or acquire the necessary data. Specifically, thermal analysis will be performed using an STA/MS to investigate the TBP degradation reactions and products. Also, the vapor pressure, density, and solubility of organic phases containing TBP diluted in dodecane will be measured before and after contact with nitric acid. These physical properties will be studied at temperatures from 50–120°C. After the data is generated, work should be done to compare the new data and literature data to existing models. The data will be used to improve the models currently used for extraction processes.

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