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Study of the Equilibrium of Nitric Acid with a Solution of TBP/IP6

Munoz Ayala Israel and Vera Roberto Carlos

Abstract

The behavior of the tri-n-butylphosphate (TBP) for a Liquid-liquid extraction (LLE) system is well known. To establish a new LLE system, the calculation of the equilibrium to establish an extraction system of TBP and inositol hexaphosphate (IP6) needs to be done. First, the change in the activity coefficient of TBP/IP6 related to the activity of water and TBP/IP6 concentration in the H₂O-TBP/IP6-dodecane system, then the degradation of nitric acid in the system should be evaluated to assess the equilibrium. The proposed system consists of a solution of 30% of TBP and 10% of IP6 in nitric acid and dodecane. As main results, we discussed the value of the dissociation degree of nitric acid, the molar and volumetric fractions, the molar activity of the organic and aqueous phases and activities coefficients.

Keywords: equilibrium, TBP, IP6, extraction system

1. Introduction

Liquid-liquid extraction ion-exchange (LLE-IE), also known as solvent extraction and partitioning, is a method to separate compounds or metal complexes, based on their relative solubilities in two different immiscible liquids, usually water (polar) and an organic solvent (non-polar) [1]. There is a net transfer of one or more species from one liquid into another liquid phase, generally from aqueous to organic. The transfer is driven by chemical potential, i.e., once the transfer is complete, the overall system of chemical components that make up the solutes and the solvents are in a more stable configuration (lower free energy). The solvent that is enriched in solute(s) is called extract. The feed solution that is depleted in solute(s) is called the raffinate. This type of process is commonly performed after a chemical reaction as part of the work-up, often including an acidic work-up [2].

From a hydrometallurgical perspective, solvent extraction is exclusively used in separation and purification of uranium and plutonium, zirconium and hafnium, separation of cobalt and nickel separation, and purification of rare earth elements etc., its greatest advantage being its ability to selectively separate out even very similar metals. One obtains high-purity single metal streams on 'stripping' out the metal value from the 'loaded' organic wherein one can precipitate or deposit the metal value.

One of the well-known applications of a LLE in hydrometallurgical techniques is the PUREX (plutonium uranium redox extraction) which is a chemical method used to purify fuel for nuclear reactors or nuclear weapons. PUREX is the de facto

standard aqueous nuclear reprocessing method for the recovery of uranium and plutonium from used nuclear fuel (spent nuclear fuel or irradiated nuclear fuel). It is based on liquid–liquid extraction ion-exchange [3].

It is not the intention of this research work to establish a new PUREX methodology but to study the equilibrium of a LLE-IE based on TBP and IP6. The behavior of TBP and nitric acid (HNO_3) in the solvent extraction process has been studied, which has detected good stability, through laboratory tests, pilot tests and plant work.

IP6 is a unique natural substance found in plant seeds. It has received considerable attention due to its effects on mineral absorption. Impairs the absorption of iron, zinc and calcium and may promote mineral deficiencies. IP6 is a six-fold dihydrogenphosphate ester of inositol (specifically, of the myo isomer), also called inositol hexakisphosphate or inositol polyphosphate (IP6). At physiological pH, the phosphates are partially ionized, resulting in the phytate anion [4].

IP6 has had a high value for the nuclear industry, as it has studied as a complement to the recovery of uranium in seawater [3] and as a bio-recovery option in mine water [5].

As has been said before, in this research just the equilibrium of the TBP/IP6 in nitric acid with n-dodecane is going to be study.

2. Results and discussions

2.1 Propose system

The purpose of this work is to study an LLE-IE system to establish a new PUREX variant. Variants refer to change in some of the original conditions which in this case is adding a new molecule to the system. Original PUREX consist in TBP with HNO_3 in a hydrocarbon. The proposed system consists in TBP with IP6 in solution con dodecane (**Figure 1**).

The IP6 presents 6 phosphates, it is water soluble and lightly soluble in ethanol and has a boiling point of 150 °C. The respective constants for calculations have been obtained from the literature [6].

The full chemical reaction with the purpose LLE-IE system is as present in **Figure 2**. It can be observed the interaction between the characteristic's actinides of

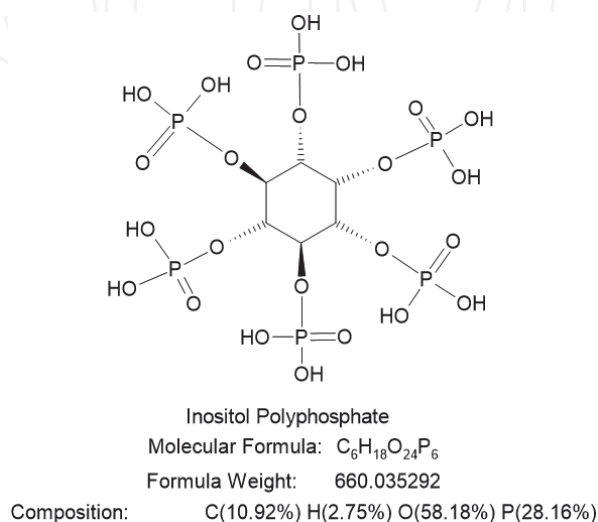


Figure 1.
Inositol polyphosphate (IP6) molecule.

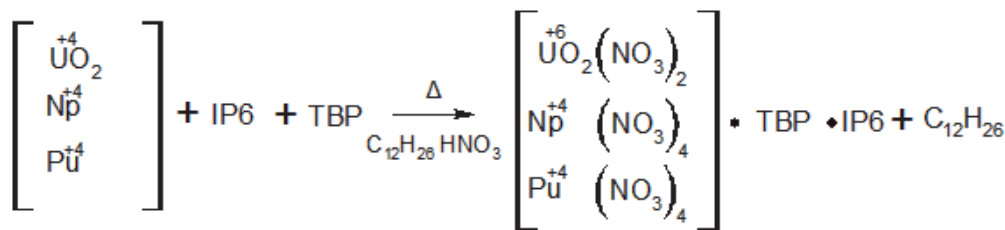


Figure 2.
 Full extraction reaction presented for the purpose PUREX system.

a spent nuclear fuel and the TBP-IP6. In this reaction, the radiolitic effects are not considered.

2.2 Effects of water on the activity of TBP/IP6 in the H2O-dodecane system

The study system comprises 30% of TBP and 10% of IP6 (TBP/IP6) in solution with water and n-dodecane.

Considering that the distribution of water in the H2O–TBP/IP6–dodecane system be described using the Equation [7] (1)

$$x_1 = K_1\varphi_2a_1 \exp \left(b_1\varphi_2^n\right) + K_2\varphi_3a_1 \tag{1}$$

Where x_i , a_i and φ_i are the molar fraction, activity, and volume fraction of the i component in solution respectively; indices 1, 2 and 3 refer to water, TBP/IP6 and dodecane respectively; in this work, by recommendation, we used $n = 2.10$; and the volume fractions of TBP/IP6 and dodecane were calculated neglecting water by:

$$\varphi_2 = \frac{x_2V_2}{x_2V_2 + x_3V_3} \tag{2}$$

$$\varphi_3 = 1 - \varphi_2 \tag{3}$$

Table 1 present the value of x_1 calculated by Eq. (1). The following constants were used: $K1 = 0.0795$, $K2 = 0.0029$ and $b_1 = 1.783$ (used for dodecane too); $V_2 = 273.8 \text{ cm}^3$ [1], $v_3 = 228.6 \text{ cm}^3$ [1], $n = 2.10$ and $k_2 = 0.1$.

a_1	x_1
1	0.044578274
0.9	0.040120447
0.8	0.035662619
0.7	0.031204792
0.6	0.026746965
0.5	0.022289137
0.4	0.01783131
0.3	0.013373482
0.2	0.008915655
0.1	0.004457827

Table 1.
 Calculate mole fractions of water in TBP/IP6 solution with dodecane.

From Eq. (1) we can derive an equation for the molar coefficient of the activity of water.

$$f_1 = \frac{1}{[K_1\varphi_2 \exp(b_1\varphi_2^n) + K_2\varphi_3]} \quad (4)$$

$$\ln f_1 = -\ln [K_1\varphi_2 \exp(b_1\varphi_2^n) + K_2\varphi_3] \quad (5)$$

The result of the Eq. (4) is a molar coefficient of $a_w f_1 = 22.432452$ and $\ln f_1 = 3.11050866$. To derive an equation for the molal coefficient of the activity of TBP, we used the cross-equation.

$$\left[\frac{\partial \ln f_1}{\partial \ln f_2} \right]_{m_1} = \left[\frac{\partial \ln f_2}{\partial \ln f_1} \right]_{m_2} \quad (6)$$

Where the derivatives with respect to the molar concentration m_2 y m_1 were calculated for constant m_1 and m_2 respectively. Differentiating (5), we obtain

$$\left[\frac{\delta \ln f_1}{\delta m_2} \right]_{m_1} = - \left\{ \frac{[K_1 \exp(b_1\varphi_2^n) + K_1\varphi_2 \exp(b_1\varphi_2^n) n b_1 \varphi_2^{n-1} - K_2]}{[K_1\varphi_2 \exp(b_1\varphi_2^n) + K_2\varphi_3]} \right\} \left[\frac{\delta \varphi_2}{\delta m_2} \right] \quad (7)$$

The value m_2 can be calculated from the mole fractions of TBP/IP6 and dodecane,

$$m_2 = \left(\frac{x_2}{x_3} \right) \left(\frac{10^3}{M_3} \right) = \left(\frac{x_{20}}{x_{30}} \right) \left(\frac{10^3}{M_3} \right) \quad (8)$$

Where x_{20} and x_{30} are the mole fraction of TBP/IP6 and diluent in anhydrous solution; $x_{30} = 1 - x_{20}$; and M_3 is the molecular mass of the solvent (170.33 g/mol). Then from (2), we obtain

$$\varphi_2 = \frac{V_2}{\left[\frac{V_2 + V_3}{\frac{x_{20}}{x_{30}}} \right]} = \frac{m_2 V_2}{\left[m_2 V_2 + \frac{V_3 x_{10}^3}{M_3} \right]} \quad (9)$$

From (9) we determinate the derivative $\delta \varphi_2 / \delta m_2$ for (7),

$$\frac{\partial \varphi_2}{\delta m_2} = \frac{V_2 V_3 x \frac{10^3}{M_3}}{\left[m_2 V_2 + \frac{V_3 x_{10}^3}{M_3} \right]^2} \quad (10)$$

Now, substituting the Eq. (10) in (7),

$$\frac{\partial \varphi_2}{\delta m_2} = \left\{ \frac{V_2 V_3 x \frac{10^3}{M_3}}{\left[m_2 V_2 + \frac{V_3 x_{10}^3}{M_3} \right]^2} \right\} x \left\{ \frac{K_1 \exp(b_1\varphi_2^n) + K_1\varphi_2 \exp(b_1\varphi_2^n) x n b_1 \varphi_2^{n-1} - K_2}{K_1\varphi_2 \exp(b_1\varphi_2^n) + K_2\varphi_3} \right\} \quad (11)$$

The right side of the Eq. (11) does not contain any value dependent on m_1 . Then, integrating the Eq. (6), we obtain

$$\ln f_2 = f_{20} - m_1 \left\{ \frac{V_2 V_3 x \frac{10^3}{M_3}}{\left[m_2 V_2 + \frac{V_3 x 10^3}{M_3} \right]^2} \right\} \left\{ \frac{K_1 \exp(b_1 \phi_2^n) + K_1 \phi_2 \exp(b_1 \phi_2^n) x n b_1 \phi_2^{n-1} - K_2}{K_1 \phi_2 \exp(b_1 \phi_2^n) + K_2 \phi_3} \right\} \quad (12)$$

Where f_{20} is the TBP-IP6 activity coefficient in a binary (considering tri-n-butylphosphate and inositol hexaphosphate as one) anhydrous solution, which can be set at 1 in the first approximation. **Table 2** presents the results of the calculation by (12).

The deviations from the ideal values are moderate and increase with the activity of water and TBP/IP6 concentration.

2.3 Dissociation of nitric acid

Nitric acid is integral to the reprocessing of irradiated fuel and other LLE, the understandings its behavior is important. Nitric acid undergoes thermal and radiolytic degradation, the products of which include nitrous acid (HNO₂) and nitrogen oxide species (NOX).

Eq. 13 shows the generic dissociation reaction of nitric acid.



The equation for calculating the degree of dissociation is as follows:

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{[C\alpha][C\alpha]}{C(1 - \alpha)} \quad (14)$$

Where K is the equilibrium constant, AB is the reagent, A⁺ and B⁻ ions (cation and anion respectively), C acid concentration and α dissociation degree. For alpha calculation purposes, we have an equilibrium constant of K = 2.598.

We will consider the dissociation of nitric acid using the polynomial Eq. (15), which has been adjusted from the data reported by [8]. In Eq. 15, the concentration of nitric acid [C] is in mol/dm³ and α the dissociation degree where $\alpha = 1$ shows a complete dissociated acid and $\alpha = 0$ a completely associated acid

a ₁	m ₁	Ln f ₂	f ₂
1	0.2438	0.05711146	0.94448879
0.9	0.2190	0.05115063	0.95013554
0.8	0.1945	0.04529659	0.95571399
0.7	0.1697	0.03940556	0.96136074
0.6	0.1449	0.03354904	0.96700749
0.5	0.1201	0.02772661	0.97265424
0.4	0.0963	0.02217066	0.9780733
0.3	0.0721	0.01655281	0.98358344
0.2	0.0474	0.01085124	0.98920742
0.1	0.0227	0.005182	0.9948314

Table 2.
Molalities of water m₁ and TBP/IP6 activity coefficient f₂ for a solution in n-dodecane.

$$\alpha = -2.64 \times 10^{-6} [C]^4 + 2.6331 \times 10^{-4} [C]^3 - 5.8558 \times 10^{-3} [C]^2 - 1.54199 \times 10^{-2} [C] + 1 \quad (15)$$

The following calculation describes the concentration of associated and dissociated nitric acid.

$$[NO_3^-] = \alpha \cdot [HNO_3]_{total} \quad (16)$$

$$[HNO_3] = [HNO_3]_{total} - [NO_3^-] \quad (17)$$

Where $[HNO_3]_{total}$ is the sum of dissociated and associated nitric acid, $[NO_3^-]$ and $[HNO_3]$ are respectively the associated and dissociated acid concentration.



It can be observed that after the 23 M the value increases again: due to the point of saturation of nitric acid and coexistence with non-associated species.

In nitric acid solutions, nitrogen oxide species, including HNO_2 , NO_2 and NO , have been observed. The presence of these species in the absence of other reactants or radiation is attributed to the thermal decomposition of nitric acid. Non-dissociated nitric acid is thermally decomposed to produce NO_2^\bullet as shown in Eq. 18; notice that this reaction is non-elementary. This thermal decomposition of nitric acid in aqueous solution has been widely reported in the literature for different concentrations, high acidity and at high temperatures (Table 3).

2.4 Calculations of the equilibrium

The calculation method used in this research work is as follow:

1. The nitric acid and water activities are calculated from the data of [8].
2. The calculation of equilibrium implies the formation of the non-hydrated $HNO_3 \cdot TBP/IP6$ monosolvate and the hydrated $HNO_3 \cdot 2TBP/IP6$ disolvate and $2HNO_3 \cdot TBP/IP6$ semisolvate of nitric acid, and the equilibrium between them obeys the mass action law.

$$x_{ij} = \frac{K_{ij} a_a^i a_2^j}{f_{ij}} \quad (19)$$

where a_a and a_2 are the nitric acid and TBP/IP6 activities, x_{ij} and f_{ij} are the molar fraction and rational activity coefficient of a solvate consisting of i acid molecules and j complex molecules (TBP/IP6). The parameter f_{ij} is calculated within the nonstoichiometric hydration concept by the equation

$$f_{ij} = \exp [h_{ij}(1 - a_1)] \quad (20)$$

where h_{ij} is the hydrate number of a solvate, and a_1 is the water activity.

3. The molar fraction of free water (nonbonded with solvates) is calculated by the equation

$$x_1 = K_1 \varphi_1 a_1 \exp (b_1 \varphi_1^n) + k_2 [K_1 \varphi_2 a_1 \exp (b_1 \varphi_2^n)]^2 + K_2 \varphi_3 a_1 \quad (21)$$

Eq. (21) is very similar to Eq. (1). As in (1), x_i , a_i , and ϕ_i are the molar fraction, activity, and volumetric fraction of the i th component in a solution. The volumetric TBP/IP6 and n-dodecane fractions are calculated without allowance for water as (2) and (3).

4. Organic phase nonideality is considered using the activity solvate coefficients calculated as

$$f_s = \exp \left[-b_2(1 - \varphi_2)^{2.1} \right] \tag{22}$$

Molarity	α	NO_3^-	HNO_3
1	0.97898485	0.97898485	0.02101515
2	0.94780094	1.89560188	0.10439812
3	0.90793309	2.72379927	0.27620073
4	0.86080276	3.44321104	0.55678896
5	0.80776805	4.03884025	0.96115975
5	0.80776805	4.03884025	0.96115975
6	0.7501237	4.5007422	1.4992578
7	0.68910109	4.82370763	2.17629237
8	0.62586824	5.00694592	2.99305408
9	0.56152981	5.05376829	3.94623171
10	0.4971271	4.971271	5.028729
11	0.43363805	4.77001855	6.22998145
12	0.37197724	4.46372688	7.53627312
13	0.31299589	4.06894657	8.93105343
14	0.25748186	3.60474604	10.39525396
15	0.20615965	3.09239475	11.90760525
16	0.1596904	2.5550464	13.4449536
17	0.11867189	2.01742213	14.98257787
18	0.08363854	1.50549372	16.49450628
19	0.05506141	1.04616679	17.95383321
20	0.0333482	0.666964	19.333036
21	0.01884325	0.39570825	20.60429175
22	0.01182754	0.26020588	21.73979412
23	0.01251869	0.28792987	22.71207013
24	0.02107096	0.50570304	23.49429696
25	0.03757525	0.93938125	24.06061875
26	0.0620591	1.6135366	24.3864634
27	0.09448669	2.55114063	24.44885937
28	0.13475884	3.77324752	24.22675248
29	0.18271301	5.29867729	23.70132271
30	0.2381233	7.143699	22.856301

Table 3.
Calculation of values for the dissociation degree of nitric acid with to molarity in the solution.

5. The molar fraction x_i is determined as

$$x_i = \frac{c_i(1 - x_1)}{\sum c_j} \tag{23}$$

where the sum $\sum c_j$ is calculated for the first time as

$$\sum c_j = c_a + c_2 + c_3 \tag{24}$$

c_a , c_2 , and c_d are the molar acid, TBP/IP6, and dodecane concentrations, respectively, and

$$c_2 = c_T - c_a \tag{25}$$

where c_T is the total complex (TBP/IP6) concentration in a solution, i.e., the formation of the monosolvate alone was initially assumed.

6. To calculate the molar fraction of free complex x_{2f} , we write the equation

$$\begin{aligned} &x_1 + x_{2f} + x_3 \\ &+ \left\{ K_{11}a_a x_{2f} f_2 + K_{21}a_a^2 x_{2f} f_2 \exp [h_{21}(a_1 - 1)] + K_{12}a_a x_{2f}^2 f_2^2 \exp [h_{12}(a_1 - 1)] \right\} \\ &* \exp \left[-b_2(1 - \varphi_2)^{2.1} \right] = 1 \end{aligned} \tag{26}$$

7. The value of x_{2f} calculated by the Eq. (26) is used to determine the molar fractions x_{ij} . The molar concentrations c_{ij} are then estimated by the equations

$$c_j = \frac{x_j d * 1000}{\sum x_i M_i} \tag{27}$$

Parameter	Value	Units
% TBP	30.00%	%
% Dodecane	60.00%	%
% IP6	10.00%	%
Molarity HNO ₃ [M]	9	mol/L
Water activity [a _w]	0.6	
Molecular weight HNO ₃	63.01	g/mol
Molecular weight Dodecane	170.34	g/mol
Molecular weight TBP	266.29	g/mol
Molecular weight IP6	660.04	g/mol
ρ HNO ₃	1.5129	g/cm ³
ρ Dodecane [d ₀]	0.73526	g/cm ³
ρ TBP	0.973	g/cm ³
ρ IP6	1.3	g/cm ³
Acid concentration [ca]	9	mol/dm ³

Table 4.
Principal input parameters and its values.

Parameter	Value
d complex TBP/IP6	1.06984
HNO ₃ Dissociation degree [α]	0.5615298
Volumetric fraction of complex [ϕ_2]	0.4
Volumetric fraction of dodecane [ϕ_3]	0.6
Molar fraction of water [x_1]	0.0257969
Molar activity coefficient water [f_1]	0.9583666
Solvate molar activity coefficient [f_s] Organic phase	0.4245719
Complex molar activity coefficient [f_2]	0.96700749

Table 5.
Principal results for the equilibrium calculation with 30% TBP/10% IP6 in.

where d is the density of a solution, and x_i and M_i are the molar fraction and mass of the i th component.

The values of c_j are used to correct the molar fractions in compliance with Eqs. (23) and (24).

The calculated acid molar concentration c_{ac} is further found as (28) and the calculated complex molar concentration c_{tc} is estimated as (29)

$$c_{ac} = c_{11} + c_{12} + 2c_{21} \tag{28}$$

$$c_{tc} = c_{2f} + c_{11} + 2c_{12} + c_{21} \tag{29}$$

Table 4 presents all the principal input parameters. The values presented in the table are the one who has been used to solve the equilibrium equations.

The concentration of the acid allowed to know the activity of water in the system, which have a value of 0.6 which represents a large amount of water to form the aqueous phase, since a water activity value equal to 1 would represent that we have the total disposition of water to hydrate.

Table 5 presents the results of the calculation in the equilibrium.

3. Conclusions

As first step in the overall objective of the study of the equilibrium in the LLE-IE, the kinetic data and constants values has been investigated to produce an initial dynamic model of the interaction of the TBP/IP6 in aqueous conditions. The effects of water in the activity of the TBP/IP6 has been evaluated. As it can be seen, the deviations from the ideal values of the molar coefficient of the system TBP/IP6 f_2 are moderate and increase with the activity of water and TBP/IP6 concentration. The density of the complex makes precipitation possible and enough availability of dissociated acid makes this complex suitable for redox reactions.

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