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Equilibrium Study for the System Tri-*n*-butyl Phosphate, Normal Paraffin Hydrocarbon, and Nitric Acid

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ABSTRACT: Tri-*n*-butyl phosphate (TBP) in diluent is generally used as a solvent for the extraction of fissile materials in the reprocessing of spent fuels by the PUREX process. The mutual solubility of TBP and water leads to the transfer of some finite amount of TBP into the aqueous phase. The distribution study of TBP between normal paraffin hydrocarbon (NPH) and nitric acid has been studied. Equilibrium curves have been generated for TBP in different concentrations of nitric acid and NPH. The distribution coefficient (K_d) is also calculated by measuring the concentration of associated TBP in the aqueous and organic phase. The effect of an inert diluent on the solubility of TBP in nitric acid is also studied. It has been found that the distribution coefficient value varies with the concentration of TBP, nitric acid, and NPH. Nitric acid partitioning between TBP and water has also been studied. The concentration of nitric acid in both phases was determined by the titration method. It has also been proven that the concentration of nitric acid varies during this equilibrium study due to 1:1 complex formation with TBP by hydrogen bonding. The equilibrium study of this TBP-NPH-nitric acid system will aid in finding out the amount of TBP in different concentrations of nitric acid in the presence of a diluent. This study will be useful in nuclear waste management generated by spent fuels of reprocessing origin.

INTRODUCTION

Equilibrium studies play a very important role in liquid–liquid extraction studies. It is an important factor which decides the distribution of solute between two liquid phases. A system is said to be in equilibrium when no mass transfer takes place between the two phases and all of the physical properties of each phase become uniform. Tri-*n*-butyl phosphate (TBP) is the most frequently used solvent in liquid–liquid extraction for nuclear fuel reprocessing. It is used as a solvent in nuclear chemistry for the recovery of the actinide elements, like Th, U, Np, and Pu. As the density and viscosity of TBP is very much similar to that of water, the separation of TBP from water becomes difficult. This problem can be solved by diluting TBP with a light, saturated hydrocarbon, such as *n*-dodecane, normal paraffin hydrocarbon (NPH), kerosene, and so forth, which reduces the density of TBP and aids in phase separation.[1]

In the TBP-NPH-HNO_3 system, TBP distributes itself between the organic and the aqueous phases. This distribution in the two phase system can be explained as follows:

TBP dissolves in NPH by dimerization[1] and can be represented by eq 1, an equilibrium reaction in the organic phase

$$x\mathrm{TBP}_{\mathrm{org}} \leftrightarrow (\mathrm{TBP})_{x\,\mathrm{org}} \qquad (1)$$

but dissolves in nitric acid due to stable equimolar, that is, 1:1 complex formation by hydrogen bonding.[2] It can be represented by eq 2, an equilibrium reaction in the aqueous phase

$$\mathrm{TBP}_{\mathrm{aq}} + \mathrm{HNO}_{3\mathrm{aq}} \leftrightarrow \mathrm{TBP}\cdot\mathrm{HNO}_{3\mathrm{aq}} \qquad (2)$$

and the equilibrium distribution coefficient (K_d) for TBP associated between the two phases can be represented by eq 3.

$$K_d = \frac{\mathrm{TBP}_{\mathrm{org}}}{\mathrm{TBP}_{\mathrm{aq}}} \qquad (3)$$

A similar type of distribution also takes place for nitric acid. Collopy and Canvedish[2] reported this equilibrium reaction. This extraction of nitric acid from aqueous solutions by TBP in NPH can be explained by eq 4.

$$\mathrm{H}^{+}_{\mathrm{aq}} + \mathrm{NO}^{3-}_{\mathrm{aq}} + \mathrm{TBP}_{\mathrm{org}} \leftrightarrow \mathrm{HNO}_3\cdot\mathrm{TBP}_{\mathrm{org}} \qquad (4)$$

while its distribution in the aqueous phase is as shown in eq 5.

$$\mathrm{HNO}_{3\mathrm{aq}} + \mathrm{H}_2\mathrm{O}_{\mathrm{aq}} \leftrightarrow \mathrm{H}_3\mathrm{O}^{+}_{\mathrm{aq}} + \mathrm{NO}^{3-}_{\mathrm{aq}} \qquad (5)$$

The above equations explain that when TBP in NPH is contacted with nitric acid two types of mass transfer take place. TBP distributes itself between NPH and nitric acid, but simultaneously nitric acid is also distributed between TBP and water.

A number of extraction studies of nitrates with TBP have been done in the past. Alcock et al.[3] have measured the mutual solubility of TBP and water in the presence of nitric acid and also in the presence of various diluents like kerosene, heptane, hexane, cyclohexane, toluene, and benzene. The partition of nitric acid between water and TBP in kerosene at various TBP concentrations has also been determined. Collopy and Cavendish[2] have published the results on equilibrium constants for the system TBP-water-nitric acid. Burns and Hanson[4] have studied the distribution of nitric acid between TBP and water. Hardy et al.[5] have also obtained data on the partitioning of nitric acid and water between aqueous nitric acid and pure TBP solutions and have also analyzed these data in the terms of the Gibbs–Duhem equation. Sagert and Lee[6] have measured the distribution of lower trialkyl phosphates like trimethyl, triethyl,

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Table 1. Characteristics of Substances Used in This Study with Their Chemical Abstracts Service (CAS) Registry Numbers

substance	CAS reg. no.	molecular formula	purity %	specific gravity $kg \cdot dm^{-3}$
tri-*n*-butyl phosphate	126-73-8	$(C_4H_9O)_3$ PO	97	0.978
normal paraffin hydrocarbon	64771-72-8	C_nH_{2n+2n} [n = 10 to 16]		0.749
nitric acid	7697-37-2	HNO_3	70	1.41

tripropyl, and tributyl phosphate between water and dodecane as a function of temperature and trialkyl phosphate concentration. Ayedi et al.[7] have presented the phase equilibrium diagram for the ternary system $H_2O-H_3PO_4-$TBP at (298.15 and 323.15) K. The bimodal curves, tie lines, and distribution curves along with the plait point by Hand's method have also been determined. The distribution coefficient of nitrous acid has been measured as a function of the nitrous and nitric acid concentrations in the aqueous phase and functions of TBP and uranium concentrations in the organic phase by Uchiyama et al.[8] The solubility of TBP in plutonium nitrate solution and in highly radioactive liquid waste (HRLW) of the PUREX process has been determined by Kuno et al.,[9] and the variation in solubility of TBP with the concentration of nitric acid and temperature has also been studied. Lawson and Hughes[10] have designed a kinetic model for extraction of nitric acid by TBP and have found that the extraction is controlled by a combination of diffusion and chemical kinetic processes. Baldwin and Higgins[11] have extracted TBP using various diluents and determined the distribution coefficient of TBP in solvents having lower miscibility. All of the above authors have mainly focused on the distribution of nitric acid between TBP and water at different temperatures and in the presence of various inert diluents, but data on distribution of TBP between nitric acid and the diluent are still not available, and the equilibrium diagram for the TBP-diluent-nitric acid system has not yet been published.

In the PUREX process, the spent fuels are typically dissolved in nitric acid, and 30 % TBP in a paraffinic diluent is used as an extracting solvent. As TBP has some solubility in nitric acid, this leads to its transfer into the aqueous phase. Removal of this dissolved TBP is of direct interest in reprocessing processes for safe disposal of this nuclear waste. Diluents like *n*-dodecane, NPH, kerosene, and so forth, affect the solubility of TBP in the aqueous phase. It is therefore of fundamental importance to study the equilibrium diagram of the ternary system TBP-diluent-nitric acid. The equilibrium study of this TBP-diluent-nitric acid system will aid in measuring the amount of TBP in different concentrations of nitric acid in the presence of diluent. The equilibrium data generated will also be useful in calculating the number of theoretical plates required for designing a column to remove dissolved TBP from aqueous waste.

The main objectives of this paper are as follows: (i) to find the equilibrium concentration of TBP at various concentration of nitric acid ranging from (0.3 to 3) M by using different amounts of diluent in TBP as the organic phase; (ii) to calculate the distribution coefficient for TBP and determination of the factors affecting its value; (iii) to measure the solubility of TBP in nitric acid as a function of diluent; and (iv) to study the variation in the concentration of nitric acid at equilibrium.

The diluent used in the present study is NPH.

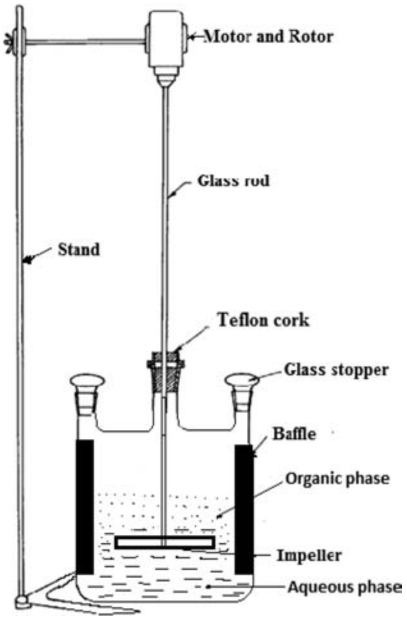

Figure 1. Schematic of the reaction assembly for equilibrium study.

EXPERIMENTAL SECTION

Materials. TBP and nitric acid were supplied by SD Fine Chemicals. NPH, also known as liquid paraffin light, was supplied by Prabhat Chemicals. All reagents used were of analytical reagent grade.

The characteristics of the reagents used in this study are shown in Table 1.

Equilibration and Phase Separation. The partition study was performed by equilibrating the organic and aqueous phases in a 1:1 ratio. A baffle reactor of 100 cm^3 capacity with a glass stirrer was used as the mixing vessel. An electrically driven motor was used for stirring the solution, and the speed was adjusted using a speed regulator as shown in Figure 1. A total of 50 cm^3 of TBP in NPH was contacted with 50 cm^3 of nitric acid at 500 rpm for around 3 h at 30 °C ± 2 °C in the reactor. The phases were allowed to separate overnight at room temperature to ensure complete separation before analysis. The settling technique was preferred over centrifugation since the latter technique might invariably result in an increase in the temperature of the solution and hence disturb the solution equilibrium.

The same procedure was repeated for different percentages of TBP in NPH ranging from 0.1 % to 100 % (v/v). The concentration of nitric acid in the aqueous phase was also varied from (0.3 to 3) M during the equilibrium study. All of the experiments were carried out in triplicate, and the average values have been reported. The deviation in the results obtained is $\leq \pm 3$ %. These deviations have been represented graphically using error bars which signify uncertainties in the measurements.

TBP Concentration Determinations. The TBP concentration in the organic phase was determined by gas chromatography (GC) and in the aqueous phase by high performance liquid

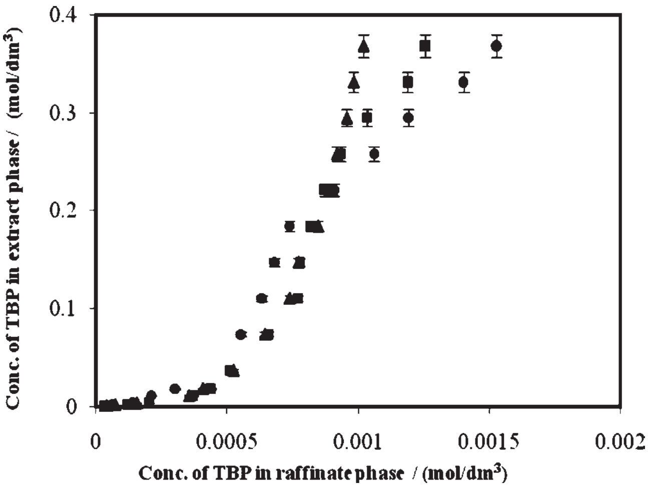

Figure 2. Graphical representation of the equilibrium data for TBP—diluent—nitric acid system. Symbols: ●, 0.3 M HNO_3; ■, 1 M HNO_3; ▲, 3 M HNO_3.

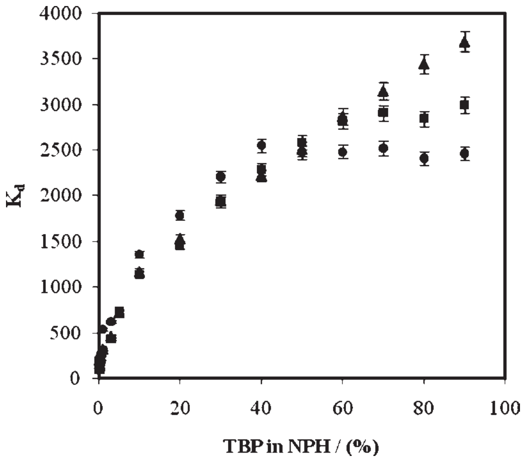

Figure 3. Effect of nitric acid and NPH on K_d values of TBP. Symbols: ●, 0.3 M HNO_3; ■, 1 M HNO_3; ▲, 3 M HNO_3.

Table 2. Effect of TBP Concentration on Distribution Coefficient of Nitric Acid

conc. Of TBP in org. phase/%	K_d for nitric acid		
	0.3 M	1 M	3 M
0.1	0	0	0
0.2	0	0	0
0.5	0	0	0
1	0	0	0
3	0	0	0
5	0	0	0
10	0	0	0.06
20	0	0.05	0.13
30	0.02	0.07	0.2
40	0.02	0.16	0.28
50	0.04	0.23	0.33
60	0.04	0.3	0.37
70	0.08	0.39	0.47
80	0.13	0.53	0.54
90	0.19	0.59	0.67
100	0.25	0.65	0.75

chromatography (HPLC). The analysis of each sample was done thrice to check the reproducibility of the results. The K_d values obtained were precise within ± 2 %.

Analysis of TBP on GC. A ThermoFisher model GC-8 gas chromatograph with a flame ionization detector (FID) was used. A 10 % OV-17 SS column with 80/100 mesh and 1/8″ × 2 m in length was used for separation. The operating conditions were as follows: column temperature, 235 °C, injector port and detector temperatures, 300 °C, and nitrogen was used as the carrier gas. Two microliters (2 μL) of the organic sample were injected into the column using a borosilicate glass syringe. A calibration curve was plotted for quantifying the amount of TBP in NPH after equilibrium.

Analysis of TBP on HPLC. A Jasco made HPLC system equipped with a R.I detector model RI-2031, an isocratic pump model PU-2080, a Rheodyne manual sample injector model 77251, and LC NET II AD box with Borwin DV software was used. A HPLC column oven model HCO-02 was used to maintain the temperature constant throughout the analysis. The HiQ sil C18 HS 4.6 mm × 250 mm in size was used as an analytical column. The mobile phase was a mixture of acetonitrile and water.

Nitric Acid Partitions. The concentration of nitric acid in both the phases after equilibration was determined by a titration method. The NaOH solution was used as a base and phenolphthalein as an indicator during the titration. The color change at the end point was from colorless to pale pink. The concentration of NaOH solution used for titration was ranged from (0.3 to 3) M depending on the concentration of nitric acid in the aqueous phase. Each sample was titrated thrice with NaOH. The uncertainty reported in the results was ≤ 0.1 %.

■ RESULTS AND DISCUSSION

The distribution coefficient was generated by varying the concentration of TBP, nitric acid, and NPH in the solution. The effect of concentration of TBP, nitric acid, and NPH on the equilibrium data for the TBP-NPH-nitric acid system has been determined and is discussed below.

Effect of TBP Concentration. The effect of TBP concentration on the equilibrium data of the TBP-NPH-HNO_3 system has been investigated. The partition of TBP between nitric acid and NPH is shown in Figure 2. The equilibrium curve was generated by varying the concentration of TBP in the organic phase ranging from 0.1 % to 100 % (v/v). It has been observed that the distribution coefficient values of TBP increase sharply with the concentration of TBP in the organic phase as shown in Figure 3. It was found that, as the concentration of TBP in the organic phase increases, more TBP is transferred into the aqueous phase, and hence, the solubility of TBP in the aqueous phase increases. The distribution coefficient values of TBP increase with increasing the aqueous phase TBP concentration because of dimerization of TBP. The results obtained are in agreement with that reported by Schulz et al.[1] They measured the distribution coefficient of TBP as a function of TBP concentration in the aqueous phase. Germain and Pluot[12] have also obtained equilibrium data for the TBP—2 M nitric acid—diluent system. They found that the distribution coefficient value of TBP increases

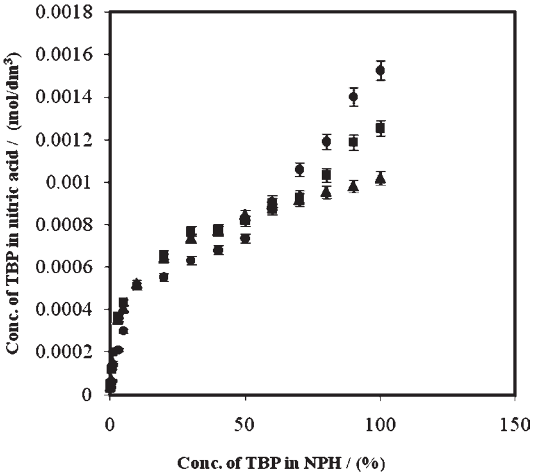

Figure 4. Effect of NPH on the solubility of TBP in the aqueous phase. Symbols: ●, 0.3 M HNO_3; ■, 1 M HNO_3; ▲, 3 M HNO_3.

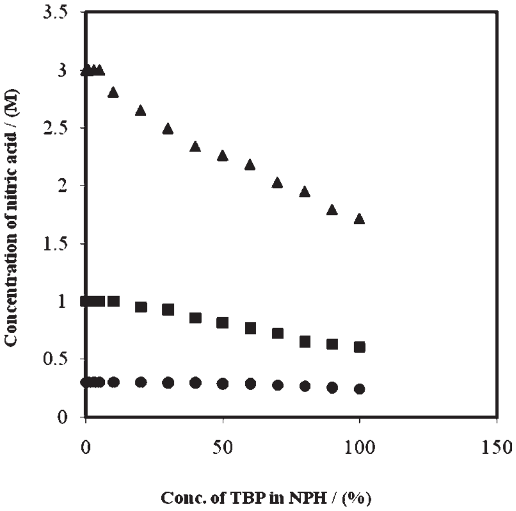

Figure 5. Variation in the concentration of nitric acid at equilibrium. Symbols: ●, 0.3 M HNO_3; ■, 1 M HNO_3; ▲, 3 M HNO_3.

sharply with the concentration of TBP in the aqueous phase. Sagert and Lee[6] reported that the distribution coefficient increases with the concentration of TBP due to aggregation of TBP in dodecane. Hence, it is confirmed from the equilibrium study that the distribution coefficient for this system depends upon the concentration of TBP in both the phases and is a function of TBP concentration in the organic phase.

Effect of Nitric Acid Concentration. The effect of nitric acid concentration on the equilibrium data of the TBP—NPH—HNO_3 system has also been studied. The equilibrium study was performed with different concentrations of nitric acid ranging from (0.3 to 3) M. The distribution coefficient values increase with the concentration of acid as shown in Figure 3. It has been assumed that this is due to a decrease in the solubility of TBP in nitric acid with the concentration of nitric acid in the aqueous phase. At lower nitric acid concentrations, more TBP is transferred into the aqueous phase, but as the concentration of nitric acid increases, this transfer process of TBP into the aqueous phase slows down. This is because of extraction of nitric acid into the organic phase by TBP which limits the solubility of TBP in the aqueous phase. Hence, it has been noticed that the distribution coefficient values increase with nitric acid concentration in the aqueous phase. The distribution coefficient value was found to be a maximum for 3 M HNO_3 and a minimum for 0.3 M HNO_3. The results obtained are in concordance with that reported by Germain and Pluot.[12] They have reported that the solubility of TBP in the nitric acid is due to complex formation by hydrogen bonding, and the distribution coefficient value rises with HNO_3 concentration due to the lower solubility of TBP in the concentrated range of nitric acid.

Effect of NPH Concentration. The influence of NPH on the equilibrium data for the TBP—NPH—HNO_3 system has also been investigated. It was found that the distribution coefficient value decreases with the concentration of NPH in the organic phase in the presence of different concentrations of nitric acid as shown in Figure 3. The effect of NPH on the solubility of TBP in nitric acid is demonstrated in Figure 4. The result obtained reveals that the presence of both NPH and nitric acid affects the distribution of TBP between the phases. The distribution of TBP in the organic phase is due to dimerization,[1] and that of nitric acid is because of hydrogen bonding.[2] The solubility of TBP in the aqueous phase is high at low concentrations of NPH but decreases with the concentration of NPH in the organic phase. NPH is a nonpolar diluent which limits the solubility of TBP in the nitric acid. The distribution of TBP in the aqueous phase is more in 0.3 M HNO_3 than 1 and 3 M HNO_3, as the solubility of TBP decreases with the concentration of nitric acid. It has also been observed from Figure 4 that the distribution curves obtained for TBP are of the different shapes in three different concentrations of nitric acid, that is, 0.3 M, 1 M, and 3 M. This difference in the curve shape is due to the extraction of nitric acid to different extents by TBP in the organic phase. The distribution coefficient values for nitric acid decrease in the order as follows: 3 M HNO_3, 1 M HNO_3, and 0.3 M HNO_3 as shown in Table 2. It is assumed that at equilibrium TBP and nitric acid both distribute themselves between the organic and the aqueous phases. It was found that, as TBP is transferred to different extents in the aqueous phase at different nitric acid concentrations, the shapes of the distribution curves are different. Hence, the mass transfer of both TBP and nitric acid governs the shapes of the distribution curves in 0.3 M, 1 M, and 3 M HNO_3. Many authors like Schulz et al.,[1] Germain and Pluot,[12] and Sagert and Lee[6] have reported similar results. They have found that the distribution of TBP in the organic phase is because of dimerization of TBP rather than the association between TBP and the diluent NPH. The distribution coefficient value increases with decreases in NPH concentration due to a lower dimerization constant.

Nitric Acid Partitioning. The change in the concentration of nitric acid at equilibrium when contacted with different percentages of TBP in NPH is shown in Figure 5. The distribution coefficient for nitric acid has been determined by measuring the amount of nitric acid in the aqueous and organic phases, and the results obtained are summarized in Table 2. It was observed that the concentration of nitric acid in the aqueous phase decreases with the concentration of TBP in the aqueous phase. The concentration of 0.3 M, 1 M, and 3 M HNO_3 reduces to 0.24 M, 0.603 M, and 1.716 M HNO_3, respectively, at equilibrium after pure TBP contact. This is due to the extraction of nitric acid by TBP into the organic phase. Acids are soluble in TBP and form strong bonds with the P=O group of TBP. It has been reported by Collopy and Cavendish[2] that TBP forms an equimolar complex with nitric acid due to hydrogen bonding which has resulted from the transfer of nitric acid into the organic phase. Hoh and Wang[13] have also studied the distribution of nitric acid between water and TBP and observed the same reason for this partition. Alcock et al.[3] agree with this complex formation mechanism and determined the solubility of nitric acid in TBP. It has also been found that the distribution coefficient value for nitric acid increases with the concentration of nitric acid due to more complex formation. Burns and Hanson[4] observed the same trend for the distribution coefficient at higher nitric acid concentration in the aqueous phase. Hence, the results obtained are in good agreement with those observed by various other investigators.

■ CONCLUSIONS

The equilibrium data have been successfully generated for the TBP−NPH−nitric acid system for three different concentrations of nitric acid. The distribution coefficient values have been found to be dependent on the concentration of TBP, nitric acid, and NPH in the system. It has also been proven that the concentration of nitric acid varies during this equilibrium study due to complex formation with TBP. The results obtained will be of prime importance in the reprocessing of spent fuels from the PUREX process and will be helpful in nuclear waste management.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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