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Effects of Diluents on the Reaction Hazards of Tributyl Phosphate with Nitric Acid

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Supporting Information

ABSTRACT: A proportion of 30 wt % of tributyl phosphate (TBP) in suitable diluents is the workhorse in the extraction of U and Pu in the plutonium uranium extraction (PUREX) process. Accelerating rate calorimetric (ARC) studies of effects of diluents on TBP behavior reveal a similar thermal behavior irrespective of the nature of diluents. The reactive thermal hazards of 30 wt % of TBP with 4N HNO₃ in different diluents show onset temperatures in the range of 105–130 °C with a significant pressure rise. Although the onset points are closer to the operating temperature range of the PUREX process, the heat rates are small. However, the process poses pressurization hazards due to the breakdown of the structure of TBP. Oxidation of butanol to butanoic acid is the main cause for exothermic behavior in all cases.

1. INTRODUCTION

Tributyl phosphate is widely used as an extractant for heavy elements.¹ Since 1957, several accidents involving TBP have been reported.^{2–5} Among those reported, Savannah River (1953)³ and Tomsk (1993)⁴ were the major accidents. In many of them, TBP with its degradation products, nitrates derived from nitric acid and heavy metals were involved.⁵ It was reported that a heavy organic layer called “Red Oil” formed as a result of the reactions at elevated temperatures between TBP and its degradation products at temperatures above 130 °C lead to increase in pressurization of the vessel that resulted in triggering runaway reactions.⁶

The studies on the thermal decomposition behaviour of TBP, its reaction with nitric acid, and the effect of diluents are inadequate. Although the conditions favorable to the thermal hazards of TBP–nitric acid system are partly available, the data on the sensitivity to thermal runaway phenomena of the chemicals involved are not available. Recently, the thermal decomposition pathway of TBP⁷ and the mechanism of red oil forming reactions and the conditions which favor the formation of red oil⁸ have been reported.

In PUREX process, diluents are used to decrease the maximum metal loading of TBP. If TBP acquires too much metal, there is a possibility for the formation of a solid metal complex, which is a critical situation for triggering accidents. Hence, 30 wt % TBP in suitable diluents is used as the workhorse for extraction of U and Pu.

Although in PUREX process plants *n*-dodecane⁹ and odorless kerosene¹⁰ are used, alternative diluents such as heavy normal paraffin (HNP)¹¹ and branched paraffin¹² (*iso*-dodecane), etc., are being explored in order to improve the extraction efficiency. The properties of the diluents such as the flash point, auto ignition temperature, lower flammability limit, and upper flammability limit (ES-1) may have significant influence in the overall thermal behaviour of the system. The thermal hazards associated with different diluents have not been

reported so far. In this manuscript, the effect of the nature and concentration of diluent on the thermal behaviour of TBP as well as their effect in the reaction between TBP and nitric acid under adiabatic conditions are discussed.

2. METHODS AND MATERIALS

TBP used here was of analytical grade obtained from Aldrich Chemicals, India. Nitric acid, *n*-dodecane, and iso-dodecane were of analytical grade obtained from M/s SD Fine Chemicals, India. Heavy normal paraffin (HNP) and odorless kerosene were obtained from M/s Flow-Tech group of Industries, India and Reliance Industries, India, respectively.

2.1. Accelerating Rate Calorimeter (ARC). The accelerating rate calorimeter (ARC) that is employed in this work to study the thermal decomposition and reactive hazards of TBP with HNO₃ is an adiabatic calorimeter for hazard evaluation of reactive chemicals. Its primary function is to allow a sample to undergo thermal decomposition due to self-heating while recording the time–temperature–pressure relationships for the runaway reactions.¹³

The significant factor in the design and construction of the ARC is the maintenance of near-perfect adiabatic conditions. In an adiabatic calorimeter, the temperature of the sample and container is continually monitored by thermocouples. The sample container system is within the calorimeter where the temperature can be changed to follow the temperature of the sample. This is done by a feedback control that detects temperature differences and adjusts power into the surrounding heaters to keep the temperature difference as close to zero as possible. The strength of the Accelerating Rate Calorimeter is that the adiabatic control is of the highest order.

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To accomplish this, the sample holder (bomb) is placed inside a nickel-plated copper jacket that is equipped with thermocouples and heating elements to produce a uniform jacket temperature and to maintain zero temperature difference between the sample holder and jacket. The sample is usually contained in a spherical metal container made from Hastelloy, a nickel alloy. On the outside of the sample container is a thermocouple; this measures container-sample temperature. The signals are fed to a control system where the sample temperature is compared to the temperatures of three thermocouples in the calorimeter, and any temperature difference is minimised by power supplied to the heaters. This is feedback control. There are three separate temperature zones, and in operation the system keeps a uniform calorimeter temperature, which can be close to a difference of 0.01 °C from the sample temperature.

In any test there is a start temperature from which the experiment begins. This is followed by a wait time to give isothermal equilibration. After this there is a seek period where the system measures temperature deviation in the system. If there is no variation in temperature, then a small heat step is programmed. This heat-wait-search step continues until there is a rise in temperature measured at the sample thermocouple which is above the chosen onset of exothermicity sensitivity. As soon as the exothermic reaction is detected, the exothermic mode is entered, and the system will force the calorimeter temperature to follow or track that of the sample as the temperature rises. Typically, as the temperature rises, the rate inwards and the reaction accelerates. The calorimeter temperature will follow the sample temperature very closely. There is a closed pressure line from the sample container to a pressure transducer, and the pressure is continually measured.

From the data, it is possible to get adiabatic temperature rise, self-heat rate data against time or temperature, the pressure, and pressure rate data. It is also possible to get the time to maximum rate or time explosion data, and it may be possible to determine full kinetic and thermodynamic information from the results.

After the ARC experiments, the residual samples in the bomb were collected and were analysed using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and gas chromatograph-mass spectroscopy (GC-MS).

2.2. Procedure for ARC Experiments. About 1 g of sample was loaded into a hastelloy bomb and its temperature raised from 50 to 450 °C incrementally by 5 °C under heat-wait-search mode, until a measurable amount ($0.02\text{ }^{\circ}\text{C min}^{-1}$) of exothermic activity was detected. For studying the reactive hazards of 30 wt % TBP with nitric acid, the acid concentration was fixed at 4N HNO₃, in order to mimic the plant condition.

2.3. Characterization Studies. **2.3.1. FT-IR.** Infrared spectra of TBP were taken in a Nicolet Impact 400 FT-IR spectrophotometer. A small drop of TBP was spread over KBr pellet into a neat thin liquid film, and the spectrum was recorded from 4000 to 400 cm⁻¹.

2.3.2. ¹H NMR. ¹H NMR was carried out using a Bruker 300 MHz multistate NMR spectrometer. D₂O was used as a solvent for the aqueous phase, and CDCl₃ was used as the solvent for dissolving the organic phase products.

2.3.3. Gas Chromatography-Mass Spectroscopy (GC-MS). The samples collected after ARC experiments were dissolved in ethyl acetate, and subjected to GC-MS analysis using Agilent 5975 MSD Inert XL. The solvent peaks were systematically

removed from the spectrum. The results were interpreted with the help of MS-NIST standard reference database library. The objective of performing analytical characterization is to identify the major chemical transformation at different diluent environments.

3. RESULTS AND DISCUSSION

3.1. ARC Study: Effect of Amount of Diluent on Thermal Behavior of TBP. To study the effect of amount of diluent on thermal behavior of TBP, *n*-dodecane was chosen, as it is the most commonly used diluent in the PUREX process. The time-temperature outputs for 30 and 70 wt % TBP in *n*-dodecane are given in Figure 1. These were plotted along with

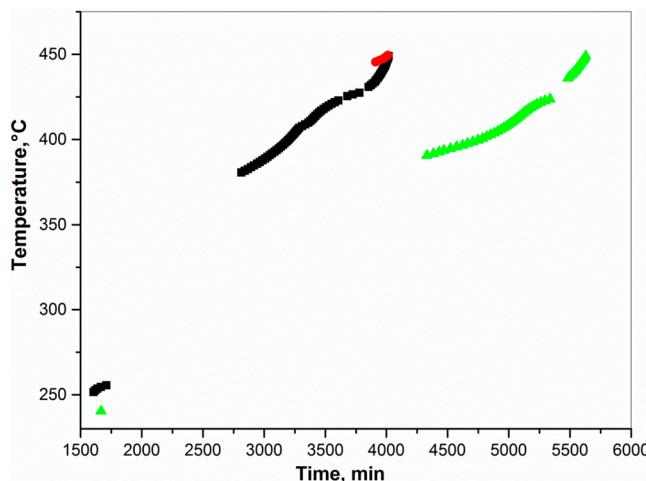


Figure 1. Time vs temperature plot of TBP: *n*-dodecane mixture in various proportions. ■, TBP; red ●, TBP 30% in *n*-dodecane; green ▲, TBP 70% in *n*-dodecane.

the neat TBP⁷ for comparative studies. TBP, when diluted with *n*-dodecane at 30 and 70 wt % levels, showed different onset temperatures (239 and 443 °C). With increase in diluent concentration, the vigor of exothermicity decreased. The self-heat rate profiles and pressure profiles are given in Figure 2 and

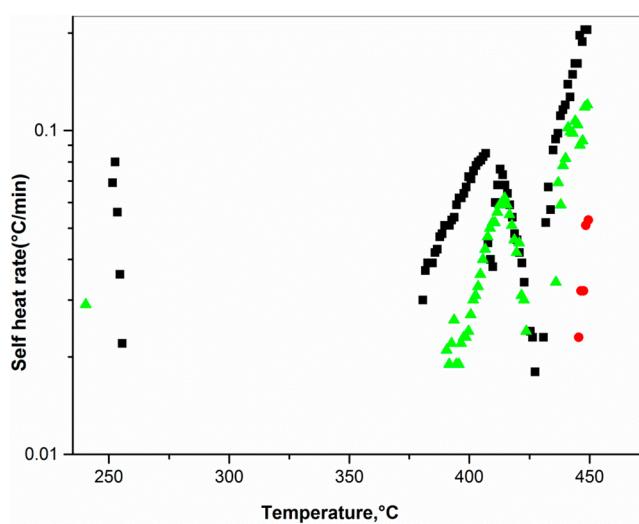


Figure 2. Temperature vs self heat rate plot of TBP: *n*-dodecane mixture in various proportions. ■, TBP; red ●, 30 wt % TBP in *n*-dodecane; green ▲, 70 wt % TBP in *n*-dodecane.

Figure 3, respectively. The decrease in the vigor of exothermicity was due to *n*-dodecane acting as a thermal

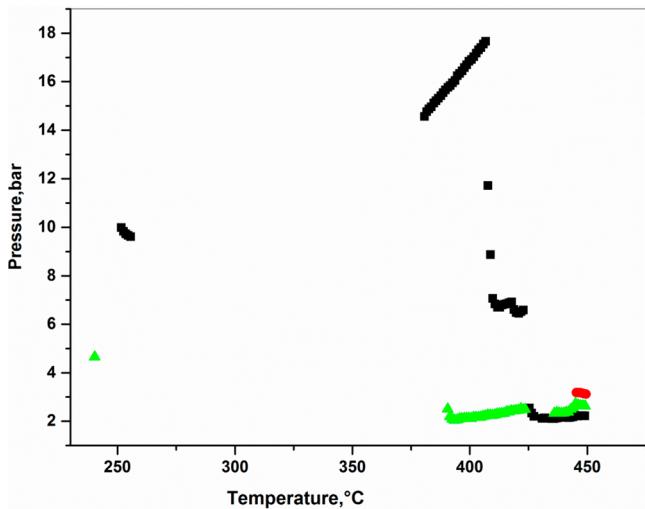


Figure 3. Pressure rise profile of TBP: *n*-dodecane mixture in various proportions. ■, TBP; red ●, 30 wt % TBP in *n*-dodecane; green ▲, 70 wt % TBP in *n*-dodecane.

sink. The pressure rise was high. On the contrary to the expectation, a decrease in pressure with temperature was noticed for 30 and 70 wt % of TBP in *n*-dodecane. An examination of the reactor contents after the reaction revealed the transformation of the reactor contents into a crud like material (change of gas and liquid phase into solid phase) which is responsible for decrease in pressure. A comparison of the trend and pattern of exothermic activity between TBP and 30 wt %, 70 wt % TBP in *n*-dodecane reveals the change in the mechanism of thermal decomposition of TBP in the presence of the diluent *n*-dodecane.

3.2. Effect of Nature of Diluents on Thermal Behavior of TBP with Nitric Acid. The time–temperature, temperature–self-heat rate, and temperature–pressure profiles are shown in Figure 4, Figure 5, and Figure 6, respectively. Reactive thermal behavior of 30 wt % TBP in different diluents with a

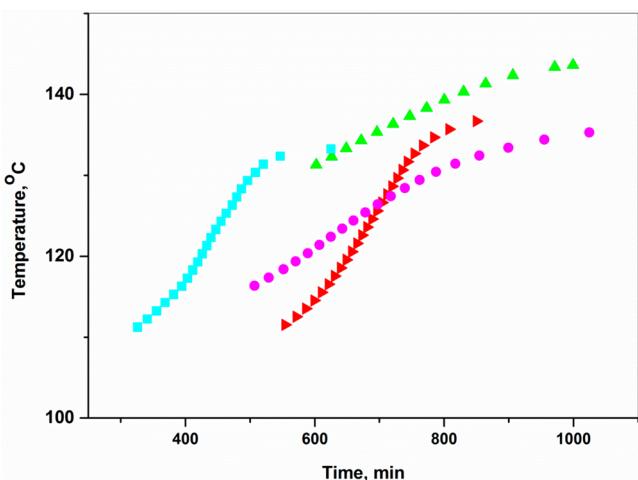


Figure 4. Comparative time–temperature plot of 30% TBP in varying diluents with 4N HNO₃ (1:1); red ▲, *n*-dodecane; green ▲, iso-Dodecane; cyan ■, heavy normal paraffin; pink ●, odorless kerosene.

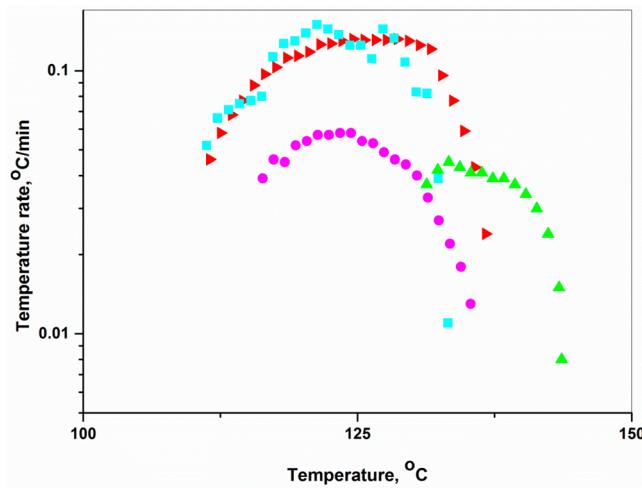


Figure 5. Comparative temperature–self heat rate plot of 30 wt % TBP in varying diluents with 4N HNO₃ (1:1); red ▲, *n*-dodecane; green ▲, iso-Dodecane; cyan ■, heavy normal paraffin; pink ●, odorless kerosene.

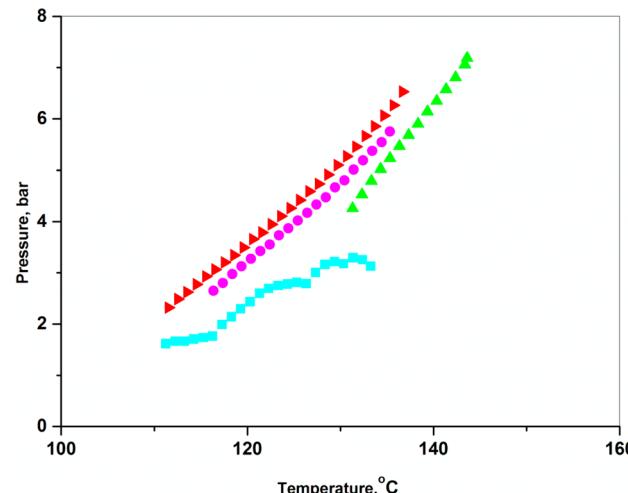


Figure 6. Comparative temperature–pressure plot of 30 wt % TBP in varying diluents with 4N HNO₃ (1:1); red ▲, *n*-dodecane; green ▲, iso-Dodecane; cyan ■, heavy normal paraffin; pink ●, odorless kerosene.

4N nitric acid in the ratio 1:1 (0.5 g of 30% TBP in diluent:0.5 g of 4N HNO₃) shows early onsets compared to the thermal behavior without the presence of acid (Figure 4). Though all of the diluents show exothermic activity, iso-dodecane showed a delayed onset of 130 °C, whereas HNP, *n*-dodecane, and odorless kerosene show onset at more or less close onset temperatures (between 110–115 °C).

The exothermic activity in the temperature range 103–150 °C may be of concern to the PUREX process since it falls in the operating temperature range. However, in process plants, when temperature exceeds the operating range, safety control systems such as the cut off of heating and triggering of emergency cooling are provided to take care of the temperature excursions. The exothermic activity recorded at higher temperature, i.e., above 250 °C for HNP and *n*-dodecane, may not be a concern to the PUREX process, as this range is quite far from the operating range.

Table 1. Summary of ARC Data of 30 wt % TBP in Varying Diluents with 4N HNO₃ (1:1)

sample no.	diluent	thermal inertia Φ	exotherm temperature range (K)			pressure (bar)		adiabatic temperature rise ΔT_{ad} (K)	heat of reaction, ΔH_r (kcal/mol)	Arrhenius parameters	
			onset T_o	final T_f	ΔT	max P at T_f	cooldown P			E_a (kcal/mol)	A (sec^{-1})
1	n-dodecane	6.77	383.5	409.5	26.0	6.8	1.8	176.5	57.5	36 532	1.26×10^{18}
2	iso-dodecane	6.79	403.3	416.6	13.3	7.5	1.65	90.4	55.2	32 557	2.18×10^{32}
3	odorless kerosene	6.77	388.3	408.3	19.9	5.8	1.7	135.1	56.4	30 867	4.87×10^{14}
4	heavy normal paraffin	6.83	283.2	406.2	23.0	8.1	1.9	157.23	57.51	33 944	2.91×10^{20}

The onset values of exotherm, adiabatic temperature rise, heat of reaction, activation energy, and Arrhenius coefficient values are summarized in Table 1. It can be noted from the table that the heat of reaction and activation energies are closer to each other, confirming a similar mechanism in operation for different diluents. The differences in reactive thermal behavior of n-dodecane and iso-dodecane are quite stark. This is due to branching in iso-dodecane leading to decreased reactivity as a result of steric hindrance.

Pressure rise profiles for reactive thermal behavior of 30 wt % TBP in various diluents with nitric acid are shown in Figure 6. A steady rise in pressure is seen for different diluents except the HNP. The pressure rise may be accounted for two reasons: (a) generation of gaseous volatile products due to thermal activity and (b) a simple pressure–temperature relationship. In this case, the former appears to be more valid, as it is shown below that reactive thermal behavior has contributed to the generation of volatile products such as CO₂, N₂, N₂O, and butyl groups.¹⁴

The maximum pressure generated is 7.5 bar for 1 g of sample in a container with 9 mL void space. Hence the pressure generated will be much higher than the design pressure. Therefore, reactive thermal behavior of 30 wt % TBP with acid appears to pose hazard to the reactor from the pressure rise angle. A close look of the cool down pressure values given in Table 1 suggests that the contribution to the maximum pressure in the system is due to the vapor pressure of liquid products of reactive thermal behavior of TBP. However, a detailed analysis is required.

3.2.2. Characterization of the Products of Thermal Activity. It has been reported in our earlier work that the reason for the exothermic behavior of TBP with nitric acid is due to the oxidation of butanol to butanoic acid.⁸ The butanol is formed from the hydrolysis of TBP in the presence of H₂O and HNO₃. Nitric acid acted as an oxidizing agent. The vigor of the reaction is proportional to the strength of the acid.⁸ Here, the influence of various diluents on the oxidative reaction between TBP and nitric acid system is analyzed using various analytical techniques such as FTIR, NMR, and GC-MS. The biphasic residue after reaction was separated into aqueous and organic phases, and appropriate solvents were used to dissolve them for characterization purposes.

3.2.2.1. FTIR. Comparative FTIR spectra of aqueous and organic phases obtained after the ARC experiments 30 wt % TBP in various diluents with 4N nitric acid are given in Figure 7 and Figure 8, respectively. The presence of –OH (3300–3500 cm⁻¹) group is clearly seen in both the aqueous and the organic phases of all samples. The broad band seen in all of the aqueous phases shows the presence of hydrogen bonding. The standard butanoic acid spectrum (ES-3) also shows a similar hydrogen bonding.

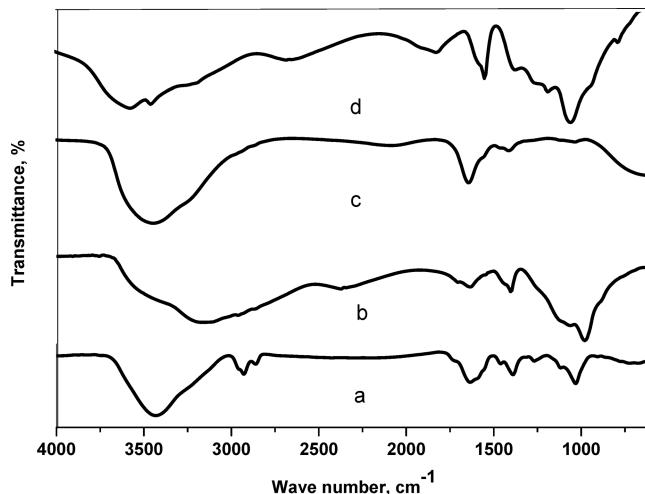


Figure 7. Comparative FTIR spectrum of the aqueous phase of 30 wt % TBP in varying diluents with 4N HNO₃ (1:1) after ARC experiments. (a) n-dodecane; (b) iso-dodecane; (c) odorless kerosene; (d) heavy normal paraffin.

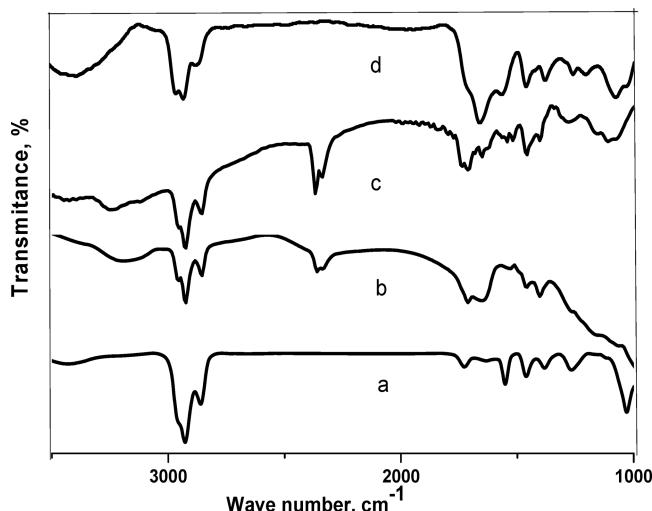


Figure 8. Comparative FTIR spectrum of the organic phase of 30 wt % TBP in varying diluents with 4N HNO₃ (1:1) after ARC experiments. (a) n-dodecane; (b) iso-dodecane; (c) odorless kerosene; (d) heavy normal paraffin.

The peaks found in the range of 1700 to 1750 cm⁻¹ corresponds to the carboxylic (C=O) group (Figure 8). The FTIR spectrum shows the presence of –COOH group in all the samples, irrespective of the nature of the diluents used. The intensities vary. The minor differences observed in the

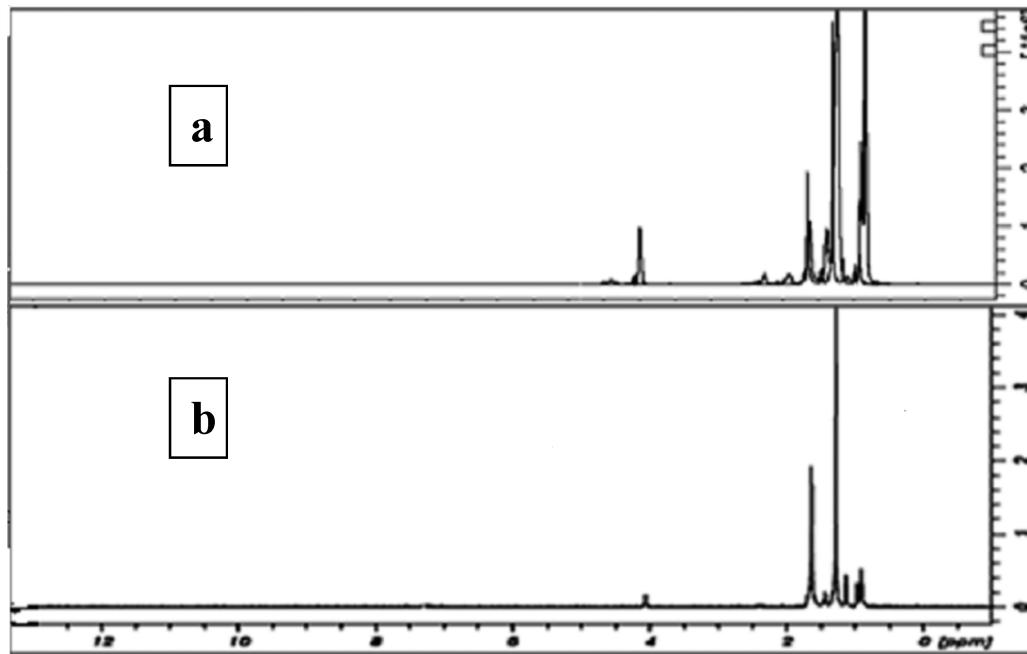


Figure 9. ¹³C spectrum of 30 wt % TBP in *n*-dodecane with 4N HNO₃ (1:1) after ARC experiments. (a) Aqueous phase; (b) organic phase.

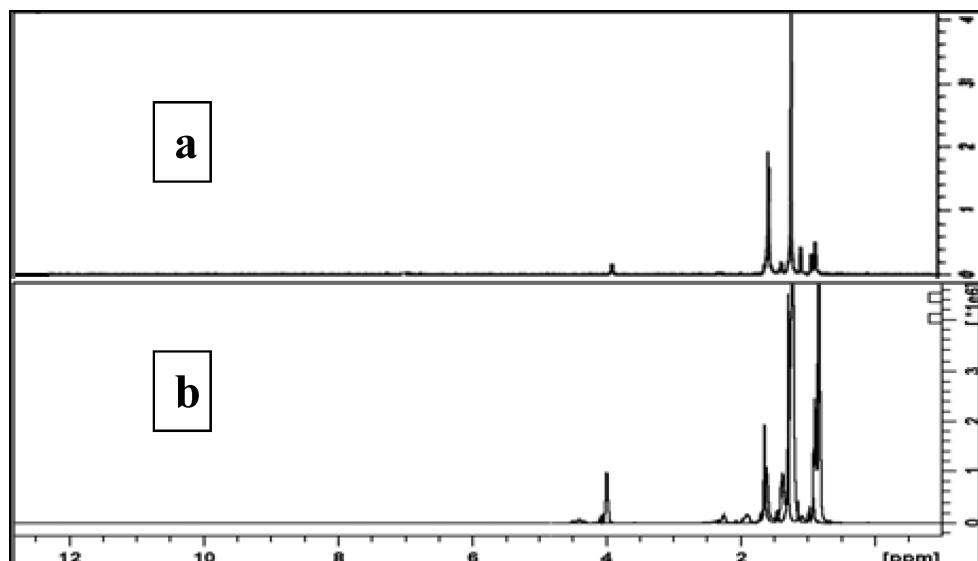


Figure 10. Comparative ¹H spectrum of 30% TBP in varying diluents with 4N HNO₃ (1:1) after ARC experiments. (a) aqueous phase; (b) organic phase.

spectrum could be due to the different hydrocarbons used as diluents.

3.2.2.2. ¹³C NMR Results. The ¹³C NMR spectral results of the aqueous and organic phases are shown in 30% TBP in *n*-dodecane with 4N nitric acid after ARC experiments. All of the chemical shifts corresponding to butanoic acid (177.3 ppm, 13.5 ppm, 38.3 ppm, 18.1 ppm) are present in the ¹³C NMR of the aqueous phase (Figure 9a).

The organic phase also shows traces of butanoic acid. The chemical shifts corresponding to TBP (63.3 ppm, 31.9 ppm, 18.6 ppm, 13.8 ppm) and *n*-dodecane (14.1 ppm, 22.8 ppm, 31.9 ppm, 29.7 ppm, 29.4 ppm) are seen in the organic phase (Figure 9b).

3.2.2.3. ¹H NMR Results. The ¹H NMR spectra of the aqueous and organic phases obtained from the ARC experi-

ment of 30% TBP in varying diluents with 4N HNO₃ (1:1) are given in Figure 10. The chemical shifts corresponding to butanoic acid (2.23 ppm, 1.60 ppm, 0.96 ppm) are seen in the aqueous phase (Figure 10a). The chemical shift corresponding to acidic –OH at 11 ppm is insignificant and hence cannot be seen in the above spectrum. The chemical shifts corresponding to TBP (4.03 ppm, 1.66 ppm, 1.33 ppm, 0.96 ppm) and *n*-dodecane (1.33 ppm, 1.29 ppm, 0.96 ppm) are seen in Figure 10b.

3.2.2.4. Gas Chromatography–Mass Spectroscopy. The GC of the aqueous and organic phases are given in ES-4 and ES-5. The gas chromatogram and mass spectrum of 30 wt % TBP in various diluents with 4N nitric acid (Figure 11) after ARC experiments shows the presence of butanoic acid (RT 2.043) irrespective of the diluent employed. The standard

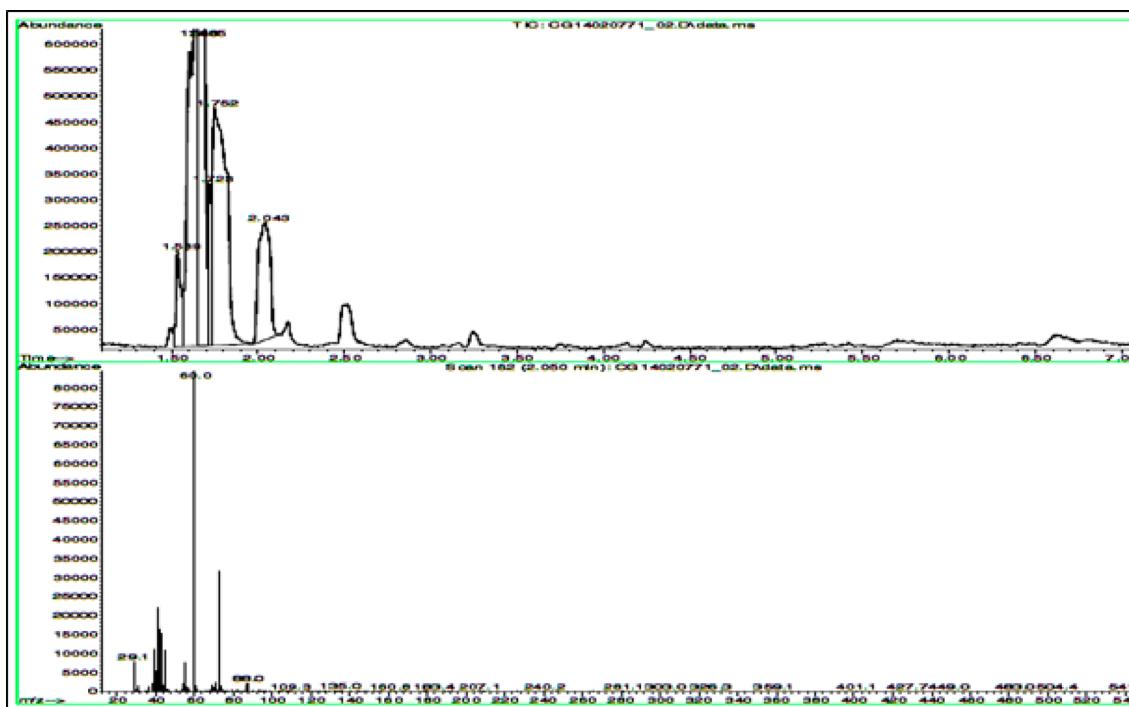


Figure 11. GC-MS of ARC residue. (a) Gas chromatogram showing butanoic acid (RT 2.043); (b) corresponding mass spectrum of RT 2.043.

butanoic acid MS of butanoic acid is presented in ES-6. The GC results also show the presence of TBP (12.818) and *n*-dodecane (5.998) in larger proportions. There are lots of other peaks observed which are probably due to the other side reactions happening in the system at elevated temperatures.

Thus, the FTIR, NMR, and GC-MS analyses of the aqueous and organic phases of the residual sample validate the predicted mechanism.⁸ The hydrolysis of TBP to butanol followed by its oxidation to butanoic acid at elevated temperatures is the main cause for the exothermic activity observed in all of the samples regardless of the diluent used.

4. CONCLUSIONS AND PROCESS SAFETY PERSPECTIVE

The accelerating rate calorimetric studies of effect of diluents on the thermal behavior of TBP with HNO₃ suggest a similar thermal behavior irrespective of nature of diluents. This study did not provide any significant lead as to a proper choice among the diluents studied for extraction of spent fuel in PUREX process. Diluents in general seem to behave as sink in reducing the vigor of the exothermicity. Further, studies on the effect of different diluents with acid reveals reactive thermal hazards due to significant pressure rise rather than the temperature excursion. Analytical characterization studies of the samples collected towards the end of the ARC studies suggested that oxidation of butanol to butanoic acid is the main cause of exothermicity. It may be noted that the observed heat rates are small; it can be well-controlled with the help of in-built temperature control strategies.

ASSOCIATED CONTENT

Supporting Information

ES-1, physical properties of diluent; ES-2, comparative time-temperature plot of 30 wt % TBP in various diluents with 4N HNO₃; ES-3, FTIR of standard butanoic acid; ES-4, GC-MS of aqueous phase obtained from 30 wt % TBP in *n*-dodecane with

4N HNO₃; ES-5, GC-MS of organic phase obtained from 30 wt % TBP in *n*-dodecane with 4N HNO₃; ES-6, standard mass spectrum of butanoic acid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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