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Effect of Radiation-Induced Physicochemical Transformations on Density and Viscosity of 30% TBP–n-Dodecane–HNO_3 System

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ABSTRACT

Radiation-induced changes in the density and viscosity of 30% TBP–n-dodecane–HNO_3 mixtures were examined. The increase in the density becomes significant with increasing nitric acid content of the solvent, $[HNO_3]_{TBP}$, and absorbed radiation dose, which concomitantly leads to a much sharper increase in the viscosity of the solvent. The extent of increase in the viscosity is significantly enhanced by gamma radiolysis and is a function of absorbed dose. These changes are attributed to radiation-induced polymerization and nitration of the hydrocarbon diluent as revealed by gas–liquid chromatography (GLC) and infrared (IR) assay of the solvent. Various possible modes of hydrogen bonding seem to play a major role in enhancing the viscosity of the system. Efficacy of solvent purification by alkaline scrub followed by alumina treatment is described in terms of the amount of

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degradation species retained in the treated solvent. Interestingly, the small amount of radiolytic species remaining in the solvent due to incomplete solvent purification causes a considerable increase in the viscosity of the solvent.

Key Words: Gamma radiolysis; TBP; Diluent; n-Dodecane; Hydrogen bonding; Viscosity; Density; Gas–liquid chromatography.

INTRODUCTION

Owing to its optimum radiation stability, extraction, and hydrodynamic property, tri-n-butyl phosphate (TBP) diluted with an inert n-paraffin mixture, has been the undisputed choice for the reprocessing of irradiated fuels by Purex process. TBP, and its complexes, with inorganic solutes are generally viscous and have a density close to that of aqueous phase. Dilution of TBP with an n-paraffin mixture (C^{10} to C^{14} chain length) causes favorable decrease in the density and viscosity of the extractant to a level optimum for the remote operation of liquid–liquid extraction process.[1]

During the extraction stage in the Purex process, the solvent comes in contact with nitric acid and intense radiation. In addition, extraction of nitric acid in the solvent also takes place.[2] Thus, the solvent is subjected to radiolysis in the presence of nitric acid. The nitric acid induced radiolytic transformations in the solvent result in the formation of a number of hydrophobic compounds that are normally not removed efficiently from the solvent by alkaline wash before recycling.[3] The major degradation products of TBP are alkyl phosphoric acids, which are relatively hydrophilic as compared to those of the hydrocarbon diluent.

The presence of such radiolytic products in the solvent alters the extraction characteristics and also brings about undesirable changes in the physical properties of the solvent.[4,5] Although there are several reports on the mechanism of extraction of mineral acids in pure TBP and TBP-diluent mixtures[6–10] based on the density and viscosity measurements, the radiation effects on the density and viscosity of the 30% TBP–n-dodecane–HNO_3 system have not been systematically investigated.

The present investigation examines such radiation-induced physico-chemical transformations of the Purex solvent as changes in the density and viscosity. The changes in these physical properties have been correlated with changes in the gas–liquid chromatographic (GLC) and infrared (IR) fingerprints of the radiolysed system.

To purify the solvent undergoing radiolytic transformations during extraction stages, it is scrubbed with an alkaline solution of sodium carbonate before recycling. The present study attempts to evaluate the efficacy of solvent purification employing sodium carbonate wash in terms of changes in the density and viscosity of the solvent after treatment.

Published research[1] suggests that the alumina treatment is effective for the removal of hydrophobic metal complexing ligands; hence, the effect of alumina treatment subsequent to alkaline cleanup has also been evaluated with respect to the improvement in the density and viscosity of the degraded solvent.

EXPERIMENTAL

Reagents and Materials

Tri-n-butyl Phosphate

Commercial TBP was purified by washing with 2% (w/v) sodium carbonate followed by distilled water. The purity of TBP was found to be higher than 99.8% by GLC assay. The n-paraffin mixture (C^{10} to C^{16} chain length) from Aldrich Inc. USA, containing 90% n-dodecane was used for dilution of TBP to 30%-n-dodecane v/v. Finely divided alumina of chromatography grade was used. All other reagents used were of AR grade.

Gamma Irradiation

A ^{60}Co source of gamma radiation with a dose rate of 5 kGy/h was used for the radiolysis of the solvent sample.

Gas Chromatographic Analysis

The irradiated solutions were analyzed using a Shimadzu model GC-9A gas chromatograph with C-R3A data processor. The resolution of multicomponent mixture of the radiolyzed solvent was performed under temperature-programmed condition on 10% SE-30 column (1.5 m × 0.32 cm) with thermal conductivity detector (TCD). The column temperature was raised from 70° to 230°C at a rate of 10°C, with a hold time of 1 min and 10 min, respectively, at the initial and final temperatures. The temperatures of injection port and TCD filament were 240°C and 260°C, respectively. Helium was used as a carrier gas at a flow rate of 50 mL/min.

The amount of di-n-butyl phosphoric acid (HDBP) formed by radiolysis in 30% TBP–n-dodecane mixture was estimated by esterifying the sample with ether solution of diazomethane prior to its gas chromatographic assay. The quantification of DBP was made by using a calibration plot.[11] The error in the estimation of HDBP is ±5%.

The degradation products of the diluent (DDP) were identified by GLC fingerprinting method as described by shaded peaks mostly eluting before the peak of TBP in Fig.1.[4,12] The net concentration (sum of the concentrations of DDP) derived from these peaks represents the total amount of diluent degradation products (DDP) formed by the radiolysis. Most of the prominent peaks (shaded) eluting after that of TBP in Fig. 1 were identified using nitrogen–phosphorous detector (NPD) and flame photometric detectors (FPD) as the signatures of high molecular weight organophosphates, referred as HMP.[13] The quantitative profiles of DDP and HMP species are obtained by using area normalization method. The net (sum) concentrations (%) evaluated from such peaks were taken as the total concentration of radiolytically formed HMP.

The estimation of the gross amount (% concentration profile) of DDP and HMP species incorporates an error of ±10% under the given resolution condition.

Infrared Measurements

A Perkin Elmer model 783 IR spectrophotometer (600 to 4000 cm^{-1}) with sodium chloride disk as a sample window was used for qualitative IR fingerprinting of the sample. Quantitative IR absorbances of test samples were measured by IR spectrophotometer model PU-9512 against 30% TBP–n-dodecane as reference using CaF_2 window with a path length of 0.1 mm.

Density Measurements

Density determinations of the solvent samples were carried out by measuring the weight of the solvent at the specified temperature using a pyknometer of 10-mL capacity. The measured density values are the mean of six determinations with an accuracy of ±0.15% for each sample.

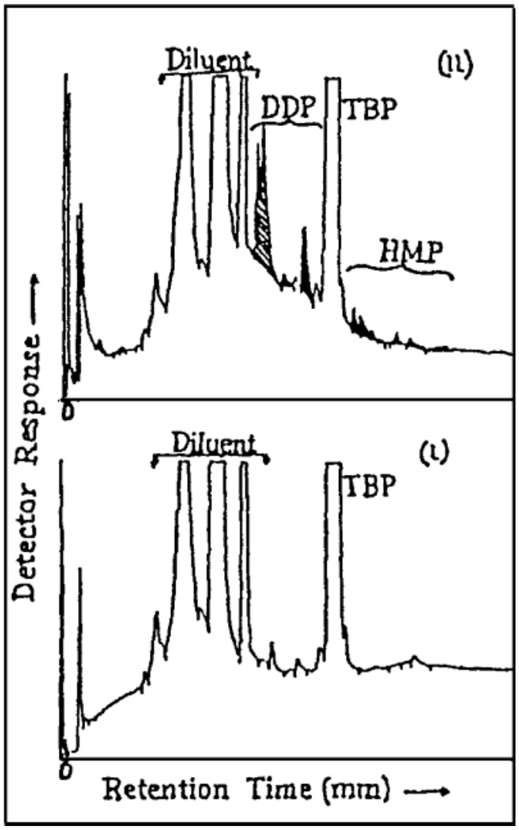

Figure 1. GLC fingerprints of (i) unirradiated 30% TBP–n-dodecane; (ii) γ irradiated 30% TBP–n-dodecane–HNO_3. Abs. dose $= 4.9 \times 10^2$ kGy. The shaded peaks represent the signatures of radiolytic products of the solvent; DDP = diluent degradation products & HMP = high molecular weight phosphates.

Viscosity Measurements

An Ubbelohde viscometer was used to measure the time of flow of the test liquid between two marked vertical positions under the force of gravity.[9] The viscosity of the solvent with respect to that of deionized water at a given temperature is calculated using the formula

$$\text{Viscosity} \quad \eta_l = [t_l \times d_l \times \eta_{w)}]/[t_w \times d_w]$$

Where, η, d, and t denote, respectively, the viscosity (c.p.), density (g/cc), and time of flow (seconds); while the subscripts l and w stand for the test liquid (l) and water. Measured viscosity values are the mean of five determinations at 23 ± 1°C with an accuracy of ±1% for each sample.

To test the effect of addition of commonly available radiolytic degradation products of the solvent on the viscosity, unirradiated 30% TBP–n-dodecane (reference) was spiked with HDBP, n-dodecanol, and their mixture. The solvent sample was also spiked individually by a mixture of DDP and HMP species obtained by fractionation of radiolyzed 30% TBP–n-dodecane–HNO_3 as described elsewhere.[13] The viscosity determinations of these solutions were measured as described previously.

Measurements of HNO_3 Concentration of the Solvent

Since the solvent extraction of actinides in the Purex process is accompanied by the extraction of nitric acid as well, it is important to equilibrate the solvent with nitric acid.

The amount of HNO_3 extracted in the solvent after equilibration (1:1 V/V; 20-min contact) with aqueous solution of nitric acid of increasing concentrations (0.5 to 3.0 M) were estimated (error ± 0.5%) by taking an aliquot in deionized water and titrating it with 0.05-N NaOH solution using phenolphthalein as an indicator. The equilibrium nitric acid concentration of the solvent is denoted as $[HNO_3]_{TBP}$.

Sample Preparation Procedure

The samples of solvent, 30% TBP–n-dodecane, equilibrated with nitric acid of different concentrations were allowed to settle overnight before subjecting them to steady-state radiolysis with incremental radiation exposure of 1.2×10^2 kGy for a maximum absorbed dose of 4.9×10^2 kGy. The samples after irradiation were subjected to GLC and IR assay. The viscosity and density of the corresponding samples were also measured.

The density and viscosity measurements were also carried out after scrubbing the radiolysed solvent with Na_2CO_3 solution (1:1 V/V, 20 min contact) as well as after subsequent purification employing sorption with alumina (0.5 g/5.0 mL solvent, 20-min contact).

RESULTS

Effect of $[HNO_3]_{TBP}$ on the Density and Viscosity

Table 1 gives the data on changes in the density of 30% TBP–n-dodecane upon equilibration with nitric acid solutions of various concentrations prior to gamma radiolysis. A slight increase in the density of the solvent is noticeable after extraction of HNO_3 in the organic phase.[2] Initial concentration of water in 30% TBP–n-dodecane before nitric acid contact was taken to be about 0.3 M.[1]

HNO_3 has higher a density than that of water. The equilibration brings about competition between water and nitric acid for available free TBP.[9] The HNO_3 extraction into the TBP takes place with the exclusion/replacement of water molecules through relatively stronger hydrogen bonding. It may be noted that TBP has a natural affinity for the uptake of water from moisture of the surrounding and the saturation solubility of water in pure TBP corresponds to 1 mole per mole of TBP. Water forms weak hydrogen bonds with the phosphoryl oxygen atom of TBP.[14]

The HNO_3 extraction in 30% TBP–n-dodecane is represented as:

$$[TBP]_{org} + HNO_{3aq} \rightleftarrows [TBP{\cdot}HNO_3]_{org} \qquad (1)$$

Based on the studies on the viscosity measurement of TBP–AMSCO–HNO_3 system, Davis et al suggested that at lower concentration of HNO_3 (0.4 M), the following reaction may occur in the organic phase.[10]

$$[TBP{\cdot}H_2O]_{org} + HNO_{3aq} \rightleftarrows [TBP{\cdot}HNO_3{\cdot}H_2O]_{org} \qquad (2)$$

$$[TBP{\cdot}H_2O]_{org} + HNO_{3aq} \rightleftarrows [TBP{\cdot}HNO_3]_{org} + H_2O_{aq} \qquad (3)$$

Table 1. Effect of $[HNO_3]_{TBP}$ on the density of 30% TBP–n-dodecane–HNO_3.

Aqueous phase acidity (M)	$[HNO_3]_{TBP}$ (M)	Density ($\times 10^{-3}$ Kg/M^3)
0.50	0.06	0.813
1.0	0.12	0.818
2.0	0.18	0.823
3.0	0.56	0.837

Density of 30% TBP–n-dodecane at 23°C = 0.810×10^{-3} Kg/M^3.

Table 2. Effect of radiolysis on density and viscosity of 30% TBP–n-dodecane–HNO_3.

	Density ($\times 10^{-3}$ Kg/M^3)			Viscosity c.p.		
	Absorbed dose ($\times 10^2$) kGy			Absorbed dose ($\times 10^2$) kGy		
$[HNO_3]_{TBP}$ (M)	0	1.2	4.9	0	1.2	4.9
0.18	0.823	0.828	0.835	1.86	1.98	2.21
0.56	0.837	0.841	0.847	1.96	2.16	2.38

Viscosity of 30% TBP–n-dodecane = 1.8 c.p; Dose rate = 5 kGy/h; Temperature = (23 ± 1)°C; 1 c.p. = 10 m poise = 10 m.N.s.m^{-2}.

Thus, the possible species resulting with increasing nitric acid extraction in the solvent are TBP (molecular weight = 266), TBP–water (284), TBP–water–HNO_3, TBP–HNO_3 (329). Major changes in the density of the solvent of c.a. 2% are due to extraction of 0.56 M of HNO_3 on contact with 3 M HNO_3.

The results of density and viscosity of 30% TBP–n-dodecane–HNO_3 system before and after gamma irradiation are presented in Table 2. The viscosity of the solvent increases more sharply than the corresponding density changes with increasing equilibrium concentration of nitric acid in the 30% TBP–n-dodecane phase (see Table 2). The exact solvent composition in terms of hydrogen-bonded species [viz. Eqs. (1 to 3)] mentioned previously is difficult to determine directly.

Radiolytic Effects

GLC Studies

The compositional changes of the solvent subjected to increasing absorbed radiation doses are better revealed by comparative study of the GLC concentration profiles of the radiolytic products. A comparison of the GLC fingerprints (see Fig. 1) of the solvent before and after radiolysis suggests the formation of species with retention times greater than that of n-dodecane (diluent) and TBP. Higher retention times of the radiolytic products than that of the parent components suggest that the species possesses higher molecular weight.

Figure 2 shows the increase in the GLC concentration (%) profiles of total degradation products (TBP + diluent) along with the net concentration

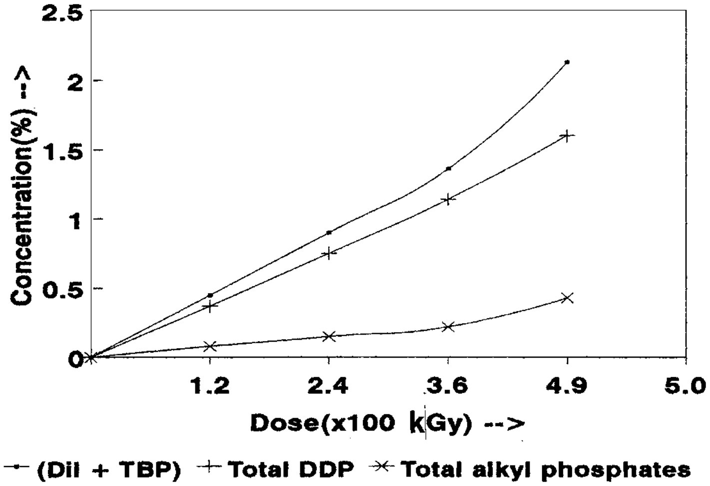

Figure 2. Dependence of GLC concentration (%) profile of the radiolytic products of 30% TBP–n-dodecane–HNO_3 on absorbed dose. Dose rate = 5 kGy/h. (i) Total degradn. products (Dil + TBP), (ii) DDP, and (iii) total alkyl phosphates = (%HDBP + %HMP).

of diluent degradation products (DDP) and total alkyl phosphates (HDBP + HMP) as a function of absorbed dose. In Fig. 2, Dil is the abbreviation used for the diluent. DDP denotes the radiolytic yield (%) of diluent degradation products induced by the presence of nitric acid in the solvent.[4] It is, thus, clearly seen that the net growth of DDP constitutes a greater fraction of the total solvent (Dil + TBP) degradation species formed as compared to that of TBP. Total solvent degradation products is defined as the sum of net (%) concentration of DDP (diluent degradation products) + net concentration of TBP degradation species (= %HDBP + %HMP = total phosphates).

Figure 3 clearly shows the dose dependence of the GLC concentration profile of TBP degradation products in terms of the concentrations of HDBP, HMP, and total phosphates (%HDBP + %HMP). Formation of various diluent degradation products (DDP) and higher molecular organophosphates (HMP) species generated by solvent radiolysis has been identified and reported elsewhere.[12,13] It may be noted that as compared to the growth of HDBP, the concentration of HMP increases much more sharply with an increasing absorbed dose. Also, the formation of HMPs are enhanced at higher doses. It constitutes a major fraction of the total radiolytic yield of organophosphates.

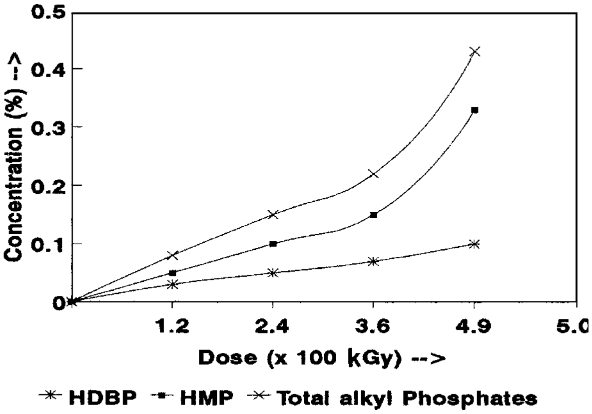

Figure 3. Dependence of GLC concentration (%) profiles of TBP degradation products (i) HDBP, (ii) HMP, and (iii) total alkyl phosphates (%HDBP + %HMP) on the absorbed dose. Dose rate = 5 kGy/h.

The contribution of H_2MBP and H_3PO_4 as the radiolytic products is excluded in the present investigation due to their incomplete resolution as well as very low relative yield. The greater lyophilicity of these species makes their elimination from the solvent easier, hence, less problematic. In this context, it may be noted that the main focus of the present investigation is to seek a correlation between the relative changes in the viscosity of the radiolysed solvent and the concentrations of degradation products. Simultaneously, the effect of solvent purification on these two parameters has also been evaluated.

IR Studies—Role of Nitric Acid

Table 3 shows IR absorbance in the wavelength range of 1510 to 1580 cm^{-1} due to nitro compounds as a function of equilibrium nitric acid concentration of organic phase and the absorbed dose. It is obvious that radiation-induced nitration of the solvent is dependent on initial $[HNO_3]_{TBP}$ and absorbed dose.

Table 4 shows that nitration products of the hydrocarbon diluent viz. nitroalkanes (RNO_2), alkyl nitrates ($RONO_2$), and alkyl nitrites, possess significantly greater density than the parent species (RH).[15] Obviously, the increase in the concentration of these nitroparaffins would inevitably result in the increase in the density of the radiolysed solvent.

Table 3. Effect of $[HNO_3]_{TBP}$ and absorbed dose on IR absorbance.

	IR absorbance in range of 1510 to 1580 cm^{-1} (peak area) at absorbed doses ($\times 10^2$) of	
$[HNO_3]_{TBP}$ (M)	2.4 kGy	4.9 kGy
0.18	1.9	3.1
0.56	2.8	5.0

Dose rate = 5 kGy/h; Cell window = CaF_2; Path length = 0.1 mm.

It must be noted that viscosity of the liquid (l) η_l is directly proportional to the density d_l of the liquid; so, in general, a higher density of the liquid is reflected in correspondingly higher viscosity of the solvent, *though there are some exceptions to this general observations*.

Thus, the research data on density (see Table 4) provide good approximations of the changes in the viscosity of the test liquid due to chemical modification of diluent (n-decane as an example) and TBP. It may be recalled that such radiation–chemical modifications of the diluent component of the Purex solvent (RNO_2 and $RONO_2$ and ROH-type species) have been

Table 4. Density values of degradation products of the diluent and TBP.[18]

Radiolytic degradation products	Density (20°C) as ($\times 10^{-3}$ Kg/M^3)	n-Paraffins homologues	Density ($\times 10^{-3}$ Kg/M^3)
n-Decane	0.726	C^{11}	0.740
n-Decyl alcohol	0.830	C^{12}	0.749
n-Decyl nitrate	0.951	C^{13}	0.757
n-Decyl nitrite	—	C^{14}	0.765
Nitrodecane	0.925	C^{15}	0.770
		C^{16}	0.774
TBP degradation products			
Di-n-butyl phosphoric acid	1.160		
Tri-n-butyl phosphate	0.976		
n-Butanol	0.810		

Reference = n-decane (as diluent); Source: *Lange's Handbook of Chemistry*, 9th ed.

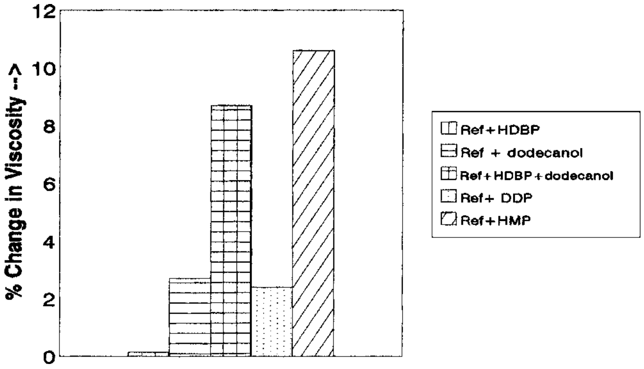

Figure 4. Effect of addition of HDBP (0.1%), n-dodecanol (0.1%) and the mixture of HDBP (0.1%) + n-dodecanol (0.1%); DDP (0.1%) and mixture of HMP species (0.1%) on the (%) change of viscosity (η) of 30% TBP−n-dodecane shown as reference (Ref).

identified by GC−MS and infrared fingerprinting by us and reported elsewhere.[12,13] Therefore, the radiolytic formation of nitroparaffins would also result in the increase in the viscosity of the solvent. Significant increase in the density of the solvent, due to radiolytic effects, is noticeable only at higher absorbed doses. Consequently, the viscosity of the radiolysed solvent is also found to increase with initial $[HNO_3]_{TBP}$ and the absorbed dose (see Table 2).

Figure 4 shows the effect of the addition of some of the radiolytic products of the solvent on the viscosity of the unirradiated solvent, 30% TBP−n-dodecane, termed as reference (or Ref.). The data indicate that the addition of 0.1% of HDBP (a TBP degradation product) or 0.1% n-dodecanol (a DDP, ROH-type species) to the reference causes only a small increase in the viscosity of the system, however, the addition of identical amounts of HDBP + n-dodecanol leads to a much larger increase in the viscosity of the reference system, i.e., 30% TBP−n-dodecane.

DISCUSSION

Factors Governing the Changes of the Viscosity: Probable Mechanism

The viscosity of the solvent increases with an increase in the molecular weight of the radiolytic species as reflected by the formation of radiolytic products with higher GLC retention times and the net growth of peaks of higher retention times than that of TBP (see Fig. 1). The increase in the viscosity of the solvent appears to be due to following radiation–chemical transformations:

1. Formation of radiation-induced nitration products (DDP) in the solvent; for example, RNO_2 (reactions 13); where R is an alkyl group.
2. Elongation of the carbon chain resulting in the formation of higher homologues of the solvent components (reactions 7, 12).
3. TBP degradation products like HDBP, H_2MBP, and n-butanol like species (reaction 4).

   $$(C_4H_9O)_3P{=}O \xrightarrow{(H^+/H_2O)} (C_4H_9O)_2(OH)P{=}O + C_4H_9OH \qquad (4)$$

   $$(\text{TBP}, \text{M.Wt.} = 266) \quad (\text{HDBP}, \text{M.Wt.} = 210) + (\text{n–Butanol}, \text{M.Wt.} = 74)$$

   In spite of a lower molecular weight in TBP degradation products, these compounds are known to be highly viscous (e.g., HDBP) due to the presence of hydrogen bonding leading to the formation of associated species. In addition, HDBP is known to undergo polymerization in organic medium,[16] e.g., to form $(HDBP)_2$ or $(HDBP)_n$. The "n" represents the number of associations of the molecules. This phenomenon may lead to increase in the viscosity of the solvent.
4. Radiolytic degradation of the solvent also results in the derivatization of TBP leading to formation of various high molecular weight organophosphates (HMP species).[13] Significant concentration of such species is formed only at higher absorbed doses (see Fig. 2). Figure 4 shows that the addition of HMP species to unirradiated solvent (reference) results in substantial increase in the viscosity (η) of the solvent.
5. In addition, intermolecular hydrogen bonding between ROH-type species (e.g., n-dodecanol, n-butanol) and radiolytic products of TBP (HDBP) appears to cause a relatively larger increase in the viscosity of the solvent. For example: it is evident from Fig. 4 that the addition of HDBP (0.1 g/L) or n-dodecanol (0.11%, a DDP species) to the control solvent sample gives rise to a 1.3 and ~2.5% increase in the viscosity of the resulting mixture, respectively. However, the addition of both the species together in identical concentration causes, much larger increase (8.1%) relatively, in the viscosity of the resulting mixture. Such a phenomenon is usually explained in terms of the existence of hydrogen bonding between HDBP and n-dodecanol (ROH species), for example, $(C_4H_9O)_2(OH)PO\cdots HOR$.

Similar types of associations are also likely to occur between hydroxylated (ROH) species, HDBP, TBP, HMP, and nitroparaffins. The large increase in the viscosity of the radiolysed solvent can be explained most plausibly by the existence of hydrogen bonding among the components of the resulting system.

Probable Radiation–Chemical Transformations

All the components of the irradiation mixture undergo radiolysis. In the present study, major radiolytic changes were due to direct radiolysis of the hydrocarbon diluent component as follows:

$$RH \rightsquigarrow [RH^*, RH^+e^-] \quad R\cdot, H\cdot, \text{ or } R'\cdot, H_2 \qquad (5)$$

$$H + RH \longrightarrow H_2 + R\cdot \quad \text{(Hydrogen Abstraction)} \qquad (6)$$

$$R\cdot + R\cdot \longrightarrow R{-}R \quad \text{(polymerization)} \qquad (7)$$

$$\longrightarrow RH + R'\cdot \quad \text{(Disproportionation)} \qquad (8)$$

R' represents a hydrocarbon species of the general formula C_nH_{2n+1}.

The higher homologues of hydrocarbon diluent are likely to give products with more carbon atoms than the parent,[4] and result in the increase in the viscosity. The increase in the viscosity with increasing chain length in the hydrocarbon series from n-decane to n-tetradecane is given in Table 5. According to eqs. (1 through 3), the solvent, 30% TBP–n-dodecane, essentially contains some amount of H_2O and nitric acid prior to γ irradiation.

Table 5. Viscosity values of n-paraffins with increasing carbon chain.

n-Paraffin		Viscosity at 20°C c. poise	Alkyl phosphate	Viscosity c. poise
n-Decane	(C^{10})	0.775	TBP	3.2
Undecane	(C^{11})	0.785	DBP	—
n-Dodecane	(C^{12})	0.947	n-Butanol	2.95
n-Tridecane	(C^{13})	1.55		
n-Tetradecane	(C^{14})	2.13		

1 centi poise = 10^{-1} m.N.s.m^{-2}; Source: *Lange's Handbook of Chemistry*, 9th ed.

The free radicals produced from their radiolysis[17] would inevitably lead to derivatization of the solvent as follows:

$$H_2O \rightsquigarrow e_{aq} + H\cdot + OH\cdot + H_2 + H_2O_2 \tag{9}$$

$$HNO_3 \rightsquigarrow OH\cdot + NO_2 \tag{10}$$

$$RH + OH\cdot/NO_2/H \longrightarrow R\cdot + H_2O/HNO_2/H_2 \tag{11}$$

$$R\cdot + R\cdot \longrightarrow R{-}R \quad \text{(Polymerization)} \tag{12}$$

NO_2 and OH· radicals react with n-paraffin diluent and their derived radicals to give nitroparaffins and alkyl alcohol as follows:

$$R\cdot + NO_2/OH\cdot \longrightarrow \underset{\text{(nitro)}}{RNO_2} \ \text{or} \ \underset{\text{(alkyl alcohol)}}{ROH} \tag{13}$$

Both RNO_2 and ROH have higher densities and viscosities than the parent RH species as explained previously (see Table 5). The effect of radiation on these compounds is, therefore, to increase the average molecular weight of the hydrocarbon as reflected by the growing concentration of high retention species in the GLC fingerprint of the solvent (see Fig. 2). This is shown by the increase in the viscosity of the radiolysed 30% TBP–n-paraffin–HNO_3 with the absorbed dose.

Effect of Solvent Purification

Figure 5 shows the effect of solvent purification on the composition profile of solvent degradation products for a given absorbed dose ($= 4.9 \times 10^2$ kGy). The inefficacy of purification of the radiolysed solvent is expressed as the (%) distribution/composition profile of degradation products (total DP, total DDP, and HMP + HDBP) retained in the solvent after alkaline cleanup followed by treatment with alumina denoted as (alk + Al). It is only HDBP, which gets almost quantitatively removed by scrubbing the solvent with sodium carbonate solution (alk ⇒ alkaline wash). The amount of HDBP retained in the solvent after solvent wash is too small for accurate determination. For this reason, Fig. 5 excludes the individual profile of HDBP and it is shown as combined (%) of (HDBP + HMP). Thus, even the combined solvent treatment fails to remove the major fraction of diluent degradation products and HMPs.

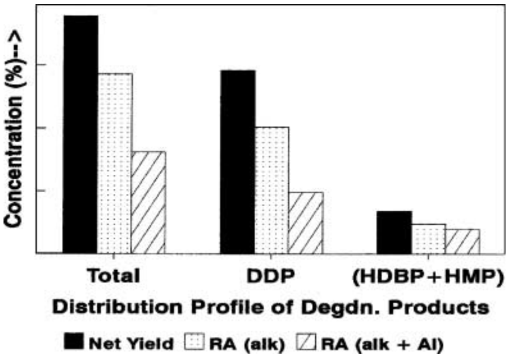

Figure 5. Dose dependence of the effect of solvent purification on the viscosity of the radiolyzed solvent Vs the retained amount of degradation products (DP). Here, Net Vis = net % increase in η and Yield of DP = % yield of total degradation products before solvent wash; while Resid Vis = (%) residual increase in η; RA of DP = the retained amount (%) of degradn. products (DP) in the solvent after purification. $[HNO_3]_{TBP} = 0.2\,M$.

Figure 6 shows the net percentage of increased viscosity {termed as [Net Vis]} and residual (%) increase in viscosity {termed as [Resid Vis]} of the radiolysed solvent, respectively, before and after solvent treatment. The (Net Vis) represents the net changes in the viscosity of the solvent, 30% TBP–n-dodecane, before its equilibration with the nitric acid and that obtained after gamma radiolysis for a given absorbed dose. Simultaneously, adjacent bars represent the corresponding amount of radiolytic species retained by the washed solvent as a function of absorbed dose. The data presented in Fig. 5 differ in absolute values from that shown in Table 2, as they belong to different series of experiments, in addition to the difference in the composition, especially, with respect to nitric acid content. However, the relativistic trends, which form the main focus of the present investigation, in both the observations, are fairly consistent. It is interesting to note that the retention of a small amount of degradation products leads to drastic increase in the viscosity of the solvent which is difficult to eliminate by liquid–liquid (alkaline cleanup) and liquid–solid (alumina treatment) equilibration processes.

It may also be noted from Fig. 6 that with the increasing extent of radiolytic degradation of the solvent, the efficacy of the solvent purification goes down. This results in a much higher rate of increase in the residual viscosity of the solvent.

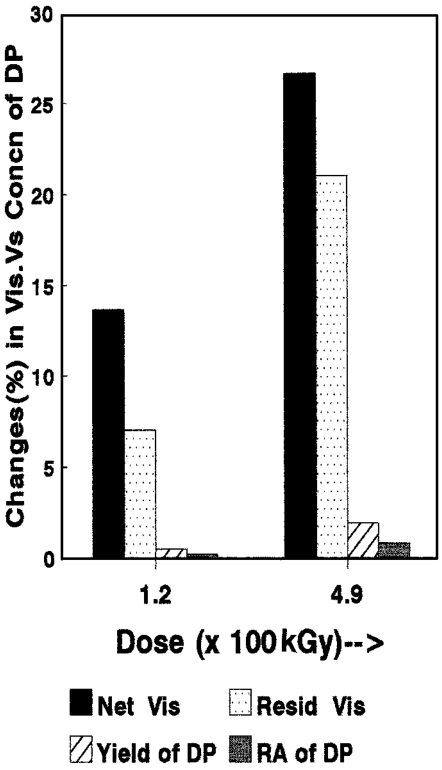

Figure 6. The effect of solvent purification on the composition profile of solvent degradation products: net yield vs the retained amount of DDP and (HDBP + HMP) in the solvent after alkaline wash RA (alk), and alkaline wash followed by alumina treatment RA (alk + Al); absorbed dose = 4.9×10^2 kGy.

The significant decrease in the viscosity of the radiolysed solvent after washing with sodium carbonate solution is mostly due to the removal of hydrophilic hydrogen bonding species containing OH groups, like butanol, and alkyl phosphoric acids, like HDBP. Alumina treatment is quite effective in removing alkyl nitrates/conjugated olefinic compounds ($1650\,\text{cm}^{-1}$) and nitroalkanes ($1556\,\text{cm}^{-1}$), as observed by comparing the IR absorbances (semiquantitative measurements) before and after alumina treatment. A small decrease in the viscosity of the solvent by alumina treatment may be attributed to the removal of the residual hydrophobic associated species of similar nature.

CONCLUSION

The present study reports the quantitative effects of radiolysis on the density and viscosity of 30% TBP–n-dodecane–HNO_3 system. The qualitative and quantitative GLC and IR studies show the nature of different types of species formed and their roles in increasing the viscosity of the Purex solvent. Significant changes in the density are noticeable upon higher uptake of nitric acid and at higher absorbed dose.

Radiolytic products of TBP, like HDBP and n-butanol, have a pronounced effect on the increased viscosity by the way of hydrogen bonding and their self-association (polymerization of HDBP). However, alkaline wash is effective in eliminating such effects through their removal.

The relatively greater increase in the residual viscosity of the solvent with absorbed dose indicates decreasing efficacy of the solvent purification step. This arises due to radiation-induced nitration and polymerization of the solvent components leading to build-up of hydrophobic and viscous species in the solvent. Even the final treatment with alumina, best known for effective removal of Pu complexing ligands from the solvent,[15] fails to completely restore the viscosity of the solvent to its original level.

A small concentration of radiolytic species causing a substantial increase in the residual viscosity of the solvent points out to highly associated and emulsifying nature of these species. During alkaline scrub of the highly radiolysed solvent, the removal of these viscous species becomes difficult due to reduced mass transfer and poor phase separation. Hence, the high level of radiolytic degradation of the solvent likely to occur during reprocessing of high burn-up fuels, especially fast reactor fuels, will lead to greater increase in the viscosity of the recycled solvent.

The present study gives an insight into the phenomenon leading to the deterioration in the quality of the Purex solvent due to accumulation of viscous and emulsifying radiolytic species.

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REFERENCES

1. Schulz, W.W.; Navratil, J.D. *Science and Technology of Tributyl Phosphate*; CRC Press Inc., 1984; Vol. 1.
2. Hesford, E.; Mc Kay, H.A.C. The extraction of acids by tri-n-butyl phosphate. J. Inorg. Nucl. Chem. **1960**, *13*, 156.
3. Tallent, O.K.; Mailen, J.C.; Pannel, K.D. *Purex Diluent Degradation*; ORNL-TM-8814; 1984.
4. Tripathi, S.C.; Bindu, P.; Ramanujam, A. *Proceedings of Indian Soc. of Analytical Scientists (ISAS) XIth Symposium (PETPHARMACHEM-95)*, Baroda, INDIA, 1995; 8, 141–143.
5. Neace, J.C. Diluent degradation products in the Purex solvent. Sep. Sci. Technol. **1983**, *18*, 1581.
6. Alcock, K.; Grimley, S.S.; Healy, T.V.; Kennedy, J.; Mc Kay, H.A.C. The extraction of nitrates of tri-n-butyl phosphates (TBP). Trans. Faraday Soc. **1956**, *52*, 39.
7. Healy, T.V.; Mc Kay, H.A.C. The extraction of tri-n-butyl phosphate. The nature of TBP phase. Trans. Faraday Soc. **1956**, *52*, 633.
8. Collopy, T.J.; Blum, J.F. Spectrophotometric evidence for complex formation in the tri-n-butyl phosphate–water nitric acid system. J. Phys. Chem. **1960**, *64*, 1324.
9. Tuck, D.G. Solvent extraction studies: IV. Viscosity measurement on the system nitric acid + tri-n-butyl phosphate. Trans. Faraday Soc. **1961**, *57*, 1297.
10. Wallace, D., Jr. Thermodynamics of extraction of nitric acid by tri-n-butyl phosphate-hydrocarbon diluent solutions. II. Densities, molal volumes, and water solubilities of TBP–AMSCO, 125-82-HNO_3. Nucl. Sci. Eng. **1962**, *14*, 159.
11. Tripathi, S.C.; Misra, S.K.; Ramanujam, A. *Proceedings of ISAS' Ist National Symp. on Recent Trends in Chromatographic Techniques*, Dec 15–17, 1989; Univ of Madras; 14.
12. Tripathi, S.C.; Bindu, P.; Ramanujam, A. Studies on the identification of harmful radiolytic products of 30%TBP–n-dodecane–HNO_3 by gas liquid chromatography. Part I: formation of diluent degradation products

and their role in Pu retention behaviour. Sep. Sci. Technol. **2001**, *36* (07), 1463.

13. Tripathi, S.C.; Ramanujam, A.; Gupta, K.K.; Bindu, P. Studies on the identification of harmful radiolytic products of 30% TBP–n-dodecane–HNO_3 by gas–liquid chromatography. Part II: formation of high molecular weight organophosphates. Sep. Sci. Technol. **2001**, *36* (13), 2863.
14. Tuck, D.G. Solvent extraction studies. II. The system nitric acid–water–tri-n-butyl phosphate. J. Chem. Soc. **1958**, 2783.
15. Mailen, J.C.; Tallent, O.K. *Clean Up of Savannah River Plant Solvent Using Solid Sorbents*; ORNL/TM-9256; 1985.
16. Burger, L.L. The neutral organophosphorous compounds as extractants. Nucl. Sci. Eng. **1963**, *16*, 428.
17. Katsumura, Y.; Jiang, P.Y.; Nagaishi, R.; Oishi, T.; Ishigure, I. Pulse radiolysis study of aqueous nitric acid solutions. Formation mechanism, yield, reactivity of NO_3 radical. J. Phys.Chem. **1991**, *95* (11), 4435.
18. Tahraqui, A.; Morris, H. Decomposition of solvent extraction media during nuclear reprocessing: literature review. Sep. Sci. Technol. **1995**, *30* (12), 2603.
19. Spinks, J.W.T.; Woods, R.J. *An Introduction to Radiation Chemistry*, 2nd Ed.; John Wiley & Sons: New York, 1976.
20. Tripathi, S.C.; Ramanujam, A.; Dhumwad, R.K. Proceedings of Nuclear and Radiochem. Symp.; Andhra Univ.: Vishakhapatnam, 1992; CA-34.

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