Hydrodynamic Properties of Tris(2-methylbutyl) Phosphate and Tri-\textit{n}-alkyl Phosphates in \textit{n}-Dodecane – A Comparative Investigation between Unirradiated and Gamma Irradiated Solvent Systems

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**ABSTRACT**

The physicochemical parameters of tris(2-methylbutyl) phosphate (T2MBP), a molecule possessing the essential characteristics required to be considered as a promising extractant in the solvent extraction stage of fast reactor fuel reprocessing, have been evaluated in the present study. In this context, the density, viscosity and interfacial tension (IFT), which are considered to be few among the important solvent selection criteria prior to its deployment in the plant scale have been measured for T2MBP in \textit{n}-dodecane (\textit{n}-DD) based systems. Similar studies have been performed with its straight chain isomer, tri-\textit{n}-amyl phosphate (TAP) as well as the widely utilized commercial extractant, tri-\textit{n}-butyl phosphate (TBP) so as to emphasize on the structural effects. Though the trends on the physicochemical behaviour of TBP based systems (temperature and ligand concentration effects) are well known in the literature, the data on TBP have been generated in the present work for comparison with the T2MBP results under similar experimental conditions. Solutions of trialkyl phosphates (TalP) in \textit{n}-DD of different concentrations have been used to generate the data on the variation of density, IFT and viscosity with the change in the ligand concentration. In addition, the transformation in their properties has been assessed after subjecting the solvents to various levels of gamma absorbed doses. Overall, it has been observed that there was no significant variation in the density of the irradiated TalPs; however, there was a significant rise in the viscosity and reduction in the IFT of the TalP samples upon irradiation. The data on the Gibbs energy change of activation of various 1.1 M TalP/\textit{n}-DD solutions have been generated by fitting their respective dynamic viscosity value as a function of temperature using Andrade’s equation. Moreover, from the IFT value, the parameters relating to the interfacial activity of TalP/\textit{n}-DD solutions have been determined using the Szyszkowski adsorption isotherm.

**KEYWORDS**

TBP; T2MBP; TAP; density; viscosity; interfacial tension

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Introduction

In a solvent extraction process, the performance of the solvent depends primarily on two important characteristics, its ability to bind specifically with the molecule or compound of interest and their degree of dispersion into the other phase for a given amount of energy. The latter in turn is determined mainly by their physical properties, such as density and viscosity of both the phases together with the interfacial tension (IFT) between them. The organic solvent should be insoluble in water so as to minimize their losses. In order to have a better separation and proper mixing of the organic and the aqueous phases leading to enhanced mass transfer efficiency, there should be a significant density difference (≥5%) and low organic-phase viscosity (<10 cp) value. Additionally, a desirable extractant should also have moderate interfacial tension. For systems with high IFT values (~>5000 mN/m), higher energy is required to create dispersion, whereas emulsion formation occurs for systems with very low IFT values (~<1 mN/m) which would take impractically longer time for separation and settlement upon phase equilibration. In addition to the phase miscibility and separation behavior of the systems, IFT also provides a picture of the extent of hydrophilicity or hydrophobicity of the extractant.\textsuperscript{[1–8]}

In addition to processing, these hydrometallurgical parameters of the system play a significant role while designing solvent extraction equipment.

Studies have shown that serious-phase separation-related issues occurred during the solvent extraction steps of nuclear fuel reprocessing due to the hydrolysis/ nitrolysis, radiolysis, and oxidation of the extractant (tri-\textit{n}-butyl phosphate (TBP)) and the diluent (\textit{n}-dodecane (\textit{n}-DD)) present in the solvent. This particular concern has been witnessed as a result of the formation of numerous irradiation products, which accumulate in the interface of the two phases as surface-active emulsifiers.\textsuperscript{[9–14]} Such degradation products can also affect their physicochemical properties as well as their extraction and stripping behaviour with actinides as well as other fission product elements.\textsuperscript{[15–21]} Few such literature works include the study on the variation of viscosity, surface tension, IFT and aqueous solubility with the change in the percentage weights of the TBP in various diluent, the effects of radiolysis on the physicochemical as well as extraction properties of TBP/\textit{n}-DD solutions.\textsuperscript{[16,22–28]}

Search for an alternate extractant having characteristics superior to TBP for spent fuel reprocessing has led to the study of the hydrodynamic properties of various amide and organophosphate molecules along with understanding their basic complexation behaviour. In this view, the viscosity and IFT of various linear and branched N,N-dialkylamides as well as tri-\textit{iso}-amyl phosphate, which has been seen to have potential reprocessing properties, have been studied in detail under varying experimental conditions such as ligand concentration, diluent purity and aqueous phase HNO\textsubscript{3} concentration.\textsuperscript{[29–34]}

\textsuperscript{[1–8]}
Another symmetric branched trialkyl phosphate molecule, which has gained its importance in the category of spent fuel reprocessing is tris(2-methylbutyl) phosphate (T2MBP), which exhibits actinide complexation power on par with TBP.\textsuperscript{35–37} Nevertheless, with its lower aqueous solubility and third-phase tendency with tetravalent metal ions compared to TBP, it opens up a scope to minimize certain hydrodynamic properties, criticality as well as red oil-related issues during its utilization in the plant scale.\textsuperscript{35,38,39} Its thermal and radiolytic degradation behaviour has been found to be similar to TBP.\textsuperscript{40,41} Moreover, in the earlier work, the alpha and gamma degradation trends of T2MBP were examined based on their extraction and stripping behaviour with Zr(IV) and Pu(IV) metal ions. A qualitative analysis of the degradation products thus obtained has also been provided using infrared and gas chromatography-mass spectrometry techniques.\textsuperscript{41} However, a study on its physicochemical properties, which is an important parameter for assessing the solvent quality, thereby identifying their suitability for reprocessing applications, is not available in the literature.

In this context, the influence of extractant concentration on the density and viscosity of water saturated and acid solvated T2MBP/n-DD solutions has been analyzed and compared with their corresponding TBP as well as tri-n-amyl phosphate (TAP)-based systems. The IFT values of the systems against water and 4 M HNO\textsubscript{3} have also been determined. Both TBP and TAP have been included in the study so as to highlight on the effects of alkyl chain length and branching of the TalP on their physicochemical properties. The structure of all the three TalPs (TBP, TAP and T2MBP) used in the present study is provided in the inset of Figure 2. The effect of gamma irradiation dose on the hydrodynamic properties of acid solvated TalP-based systems has been

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Variation of IFT values for water saturated TalP/n-DD (against water) with respect to the change in TalP concentration at 303 K.}
\end{figure}
estimated. From the IFT values of the extractants in n-DD solutions (<0.05 M), the interfacial activities of the system have been evaluated using Szyszkowski adsorption isotherm. The variation of viscosity of acid solvated solutions 1.1 M TalP in n-DD prior to and after exposing with gamma radiation was measured with respect to the change in temperature (298.15–323.15 K) and the data were fitted with Andrade’s equation so as to deduce the Gibbs energy change of activation of various systems.

**Experimental**

**Materials**

The extractant, TBP (98% purity) and diluent, n-DD (≥99% purity) purchased from Sigma Aldrich, USA were used for the extraction studies. The other extractants, TAP and T2MBP, used in the current work were synthesized by the condensation reaction between phosphoryl chloride and stoichiometric equivalent of 1-pentanol and 2-methyl-1-butanol, respectively. The reaction was carried out in n-heptane solvent medium in the presence of pyridine as the base. Additional details on the preparation as well as purification steps involved in the synthesis of the extractant are provided elsewhere.\[^{36,42}\]
purity of T2MBP and TAP used for the experiment was found to be > 99% by Gas Chromatography technique (SI-1 and SI-2). Analytical reagent grade nitric acid used for the experiments was purchased from Rankem, India.

Method

**Preparation of solutions and irradiation**
Solutions of TalP (TBP, TAP and T2MBP) in \( n \)-DD of varying concentration (0.05 M – 3.6 M) were prepared. Acid-solvated solutions of TalP/\( n \)-DD were prepared by equilibrating equal volumes of TalP/\( n \)-DD and 4 M HNO\(_3\) solutions in a glass stoppered tube for 10 min using a magnetic stirrer. A constant temperature of 303 K was maintained throughout the study by placing the tube in a water bath. The system was left undisturbed after equilibration, and the phases were allowed to separate. This is followed by the replacement of the aqueous phase with the same volume of fresh nitric acid (4 M) stock. The above step was performed since a small amount of HNO\(_3\) gets extracted into the TalP/\( n \)-DD phase and it was repeated thrice in order to achieve an equilibrium aqueous phase HNO\(_3\) concentration of 4 M. The corresponding organic phase solvated with HNO\(_3\) was used for the determination of physicochemical properties. In order to prevent the acid hydrolysis of the solution, the study using acid solvated solutions were carried out within 1 day after the preparation of the solution.

The study also involved the irradiation of solvents (extractant solution in \( n \)-DD) after pre-equilibrating with 4 M HNO\(_3\) to the required level of absorbed dose (100, 500 and 1000 kGy) using a \(^{60}\)Co gamma irradiation chamber, standardized using Fricke dosimetry, that provides a dose rate of 2.3 kGy/h. Subsequently, the radiolytically degraded samples obtained from the irradiator were utilized to carry out the experiments, which involve the measurement of density, viscosity and IFT.

**Determination of density and viscosity**
The density and viscosity of various water saturated and acid solvated TalP/\( n \)-DD solvents (irradiated and unirradiated) were measured at 303 K using micro viscometer Lovis 2000ME coupled with densitometer DMA 4500 M. The instrument calibration has been carried out with dry air and distilled water at 1 atm each time prior to the measurement of the samples. The measured density value has a standard deviation of \( \pm 1 \times 10^{-4} \) g/mL while that of viscosity is \( \pm 0.15–0.25\% \).

**Determination of interfacial tension**
For the IFT measurement using Drop Weight Technique, the aqueous phase (water or 4 M HNO\(_3\)) was taken in a Agla syringe, which has been attached to a glass capillary tube and a micrometer tip, capable of releasing a small volume
drop slowly into the corresponding organic phase. The organic solution was taken in a glass vial which is placed inside a water bath to maintain a constant temperature. The weight of glass vial was measured using a balance before and after dispensing a known number of drops from which the weight of single drop was calculated. Thus, by estimating the densities of both the phases \( (\rho_{aq} \text{ and } \rho_{org}) \) after equilibration, capillary tip radius \( (r) \), volume \( (V) \) and radius \( (R) \) of the aqueous phase drop at the moment of separation, the interfacial tension \( (\Gamma) \) can be evaluated by the following equation (Equation (1))\(^{43-45}\)

\[
\Gamma = \frac{[V \times (\rho_{aq} - \rho_{org}) \times g]}{[2 \times \pi \times r \times f_s]}
\]  

(1)

where \( g \) is the acceleration due to gravity and \( f_s \) is the Smith’s correction factor, which is given by

\[
f_s = (1 - \frac{r}{R})
\]  

(2)

The values shown are the mean of ten about replicate readings and have a relative standard deviation of \( \pm 0.1 \) mN/m. In order to validate the values obtained in the present study, IFT value of 100% TBP was measured at 293.15 K and obtained to be 8.1 mN/m, which is found to be in accordance with the literature reported data (8.0 mN/m).\(^{8,46}\) Similarly, the IFT of \( n \)-DD was measured and observed to be 52.5 mN/m at 303 K, which is found to be on par with the earlier reported data i.e. 52.1 mN/m under identical condition.\(^{47}\)

Results and discussion

Physicochemical parameters of TalPs before gamma irradiation

Effect of extractant concentration on IFT for water saturated TalP/\( n \)-DD

The results obtained from the IFT studies of water saturated TBP, TAP and T2MBP solutions in \( n \)-DD measured against water are shown in Figure 1. It can be seen from the plot that there is a reduction in IFT value with the increase in the concentration of the extractant for all the three systems. It can be understood that the TalP molecules containing both hydrophilic \( (P = O) \) and hydrophobic (alkyl chain) components are surface active in nature. Therefore, these molecules prefer to be at the interface of the two layers, allowing the phases to mix more easily, and lowering the IFT value. This explains the observed decreasing trend in the magnitude of IFT with the increase in concentration of the extractant. In other words it can also be justified based on the decrease in the overall hydrophobicity with the increase in the organic phase extractant concentration. Earlier reports on the change in the IFT data as a function of ligand concentration have shown similar trend for \( N,N \)-dialkyl amides based solvents.\(^{29,32}\)
It can also be noticed that among TBP, TAP and T2MBP-based systems, for a particular extractant concentration, the IFT value for TBP system was found to be the least. Though TalPs, in general, are relatively hydrophilic in contrast to the non-polar n-DD, increase in the size of the TalP molecule due to the addition of three − CH₂ groups, in the case of TAP and T2MBP enhances their hydrophobicity when compared to TBP/n-DD system. Consequently, the values of IFT of TBP/n-DD•H₂O based system are found to be lower than TAP/n-DD•H₂O and T2MBP/n-DD•H₂O. Also, among TAP and T2MBP, due to the higher molecular surface area resulting in prominent Van der Waals dispersion forces for TAP, the IFT values of the linear isomer (TAP) were found to be higher than the corresponding branched one (T2MBP).

**Effect of extractant concentration on IFT for acid solvated TalP/n-DD**

For all the three systems, the IFT was found to be higher when the equilibrium aqueous phase is HNO₃ instead of H₂O (Figure 2a–c). This is due to the formation of acid solvated species (TalP•HNO₃) in the organic phase upon the equilibration of TalP/n-DD phase with HNO₃, which are considered to have lower interfacial activity than neat TalP molecule. The neutral acid-extractant complex would migrate towards the bulk of TalP/n-DD phase and will not be readily available at the interface. [29,48] Hence, a relatively large amount of energy would be required to drag the acid-solvated molecule from the interior of the organic phase to the interface, and thus leading to higher IFT values. The IFT value for acid solvated TalP/n-DD systems is found to decrease with increasing TalP concentration that is similar to the trend observed for water saturated systems.

**Effect of concentration of TalPs on density and viscosity**

The viscosity of water saturated TalP/n-DD (0.2 M-3.1 M) were measured at 303 K (Figure 3). It can be noted from the plot that in general the viscosity increases with the increase in extractant concentration, and also the values are higher for TAP and T2MBP than that of the TBP. This is due to the relatively higher molecular mass resulting in more significant van der Waals interaction in the case of TAP and T2MBP-based systems. Similarly, earlier reports show that there is a linear relationship of extractant concentration on the density for water saturated TalP/n-C₁₂H₂₆. [49] However, there is no considerable difference between the density of TBP, TAP and T2MBP system in contrast to the viscosity value. Table 1 provides a comparative data on the density of water saturated and acid solvated solutions of 1.1 M TalP/n-DD at 303 K and the influence of temperature of the respective systems in the temperature ranging from 298 to 323 K is provided in Figure 4. It can be observed that there is a marginal increase in the density and considerable increase in viscosity (Figure 5a–c) of the solvent after nitric acid is being extracted into the organic phase when compared to H₂O equilibrated systems. The reason for this is due to the replacement of water molecules with comparatively more denser and viscous nitric acid molecules through relatively
stronger hydrogen bonding upon the equilibration of the solution with 4 M HNO₃. Moreover, it has been observed in molecular scale that the organic phase (TalP/n-DD) loaded with HNO₃ forms reverse micelle like structure consisting of the hydrophilic part having H₃O⁺, NO₃⁻, H₂O as well as P = O group of the TalP

**Figure 3.** Variation of viscosity of water saturated TalP/n-DD with the change in TalP concentration at 303 K.

**Table 1.** Density of water saturated and acid solvated solvent systems at 303 K.

| System            | Density (g/cm³) | Water saturated | Acid solvated |
|-------------------|----------------|----------------|---------------|
| 1.1 M TalP/n-DD   |                |                |               |
| TBP               | 0.8092         | 0.8316         |
| TAP               | 0.8145         | 0.8401         |
| T2MBP             | 0.8118         | 0.8319         |

**Figure 4.** Influence of temperature on the density of water saturated and acid solvated 1.1 M TalP/n-DD solvent systems.
and the hydrophobic alkyl part of TalP. There exists self-association and aggregation between the reverse micelle due to the polar-polar interaction. The extent of this aggregation is observed to increase with the increase in the extractant as well as HNO\textsubscript{3} concentration in the organic phase which can also be correlated with the rise in viscosity in bulk scale\textsuperscript{[50,51]} Thus, the observed rise in viscosity is more predominant for samples with higher extractant concentration.

**Physicochemical parameters of TalPs after gamma irradiation (100, 500 and 1000kGy)**

**Influence of gamma irradiation on IFT for acid solvated TalP in n-DD**

The IFT values obtained after irradiating TBP, TAP and T2MBP based solvents (pre-equilibrated with 4 M HNO\textsubscript{3}) for different levels of gamma dose (100, 500 and 1000 kGy) are shown in Figure 6a–c, respectively. It can be observed that when compared to the unirradiated samples, there is only a negligible decrease in the IFT values after irradiating the samples for 100 kGy. However, there is a drastic reduction observed in the IFT values of samples after irradiating it for a dose of 500 and 1000 kGy. Earlier studies have shown that the major radiolytic degradation products of hydrocarbon diluent are nitro derivatives of alkanes and alkenes, alkyl nitrites, alcohols, carboxylic acids etc.\textsuperscript{[11,52]} Also, the extractant (trialkyl phosphate) degrades into dialkyl phosphate, monoalkyl phosphate and phosphoric acid.\textsuperscript{[11]} The reduction in the IFT values after gamma irradiation could be justified due to the formation of these hydrophilic degradation products in the organic phase, which have better interfacial activity when compared to the parent compounds. This decrease in IFT of the solvent system upon irradiation would affect the phase separation time at larger scale.

**Influence of gamma irradiation on density and viscosity for acid solvated TalP/ n-DD**

It can be noted from Figures 7 and 8 that there is a rise in the density and viscosity of the samples upon irradiation and the magnitude of the increase in viscosity is significant for samples with higher ligand (TalP) concentration. It can be observed that the density decreases with the increase in temperature for irradiated 1.1 M TalP/n-DD•HNO\textsubscript{3} (Figure 8). It can also be deduced from Figure 7 that the viscosity enhancement is directly proportional to the absorbed dose. The sharp rise in viscosity of the irradiated samples with the increase in the absorbed dose levels can be related to the chemical transformations of the parent compound under gamma radiation. One such reason is the formation of nitration products of the hydrocarbon diluents, n-DD (RNO\textsubscript{2}, RONO\textsubscript{2}) which are considered to have larger molar mass, intermolecular interaction and higher density value than n-DD. Secondly, the production of TalP degradation products like dialkyl phosphate, monoalkyl phosphate and
alcohol species upon irradiation might also be a cause for the viscosity rise. Though the formed radiolytic products of TlP have been observed to possess lower molar mass than their corresponding parent TlP compound, the hydrogen bonding ability of dialkyl phosphate, monoalkyl phosphate as well as the alcohol-based species such as n-butanol, n-pentanol, 2-methyl-1-butanol, n-dodecanol could possibly contribute for the increasing viscosity of the overall system. Additionally, the influence of gamma irradiation dose on the IFT and viscosity of acid solvated 1.1 M TlP/n-DD systems is provided in Figure 9 for a better understanding.

**Effect of alkali washing on the physicochemical properties of gamma irradiated 1.1M TlP systems**

In order to remove the degradation products, 5 M NaOH washing has been performed on 500 kGy irradiated 1.1 M solutions of TlP in n-DD. The physicochemical properties i.e., density, viscosity and IFT of 500 KGY irradiated TlP (TBP, TAP and T2MBP) samples were measured. The sample was then equilibrated with equal volume of 5 M NaOH for 1 h and then subsequently washed several times with distilled water. After confirming that the alkali has been washed completely, the samples were again subjected to density, viscosity and IFT measurements. On comparing the results (Table 2), it can be understood that
the density and viscosity decrease, while the IFT value increases after 5 M NaOH washing. However, the physicochemical data of alkali washed samples still vary from their corresponding unirradiated systems, which could be attributed due to the decrease in the extractant concentration or the presence of certain degradation products that cannot be eliminated by alkali wash. Similar studies have been carried out earlier to comprehend the effect of alkali washing on 1000 kGy acid solvated 1.1 M TalP/n-DD systems.\textsuperscript{[41]} The washed samples were characterized and their densities as well as acid extraction data were analyzed. It can be concluded from the results obtained from the earlier reported and present study that though certain nitro- and carbonyl-based degradation products have been removed, complete regeneration of the samples is not possible by single contact of NaOH washing.

**Variation of viscosity with temperature for 30% TalP/n-DD systems**

The dynamic viscosity of acid solvated 1.1 M solutions of TBP, TAP, and T2MBP in n-DD (before and after irradiation) as a function of temperature ranging from 298.15 to 323.15 K was measured. Viscosity ($\eta$) is a rate
phenomenon and thermodynamically it can be related to the molar volume \( (V) \), Gibbs energy change of activation for viscous flow \( (\Delta G^*) \) and temperature \( (T) \) using the following Arrhenius rate equation (Equation (3)).

\[
\eta = \frac{N_0 h}{V} \times e^{-\frac{\Delta G^*}{RT}}
\]

where \( N_0 \) is Avogadro’s number, \( h \) is Plank’s constant and \( R \) represents the Gas constant.

It is also to be noted here that various models have been suggested in the literature for predicting the viscosity of mixture of binary and ternary systems which are non-ideal in nature due to the presence of intermolecular interaction in such systems.[53–56] Shekar Kumar and S. B. Koganthi[54] in their reported work have successfully predicted the dynamic liquid mixture viscosities for binary TBP/\( n \)-DD as well as ternary water saturated TBP/\( n \)-DD (TBP/\( n \)-DD•\( H_2O \)) using Grunberg-Nissan model and their corresponding parameters of interaction were evaluated.[55] Moreover, the dynamic viscosity data reported by Mole et al[57] for temperatures varying from 208.15 K to 338.15 K, has also been modelled on the basis of an extension of the Andrade equation. Earlier results have shown that an Arrhenius plot (\( \eta \) vs 1/T) for the

**Figure 7.** Comparison of viscosity values of irradiated and unirradiated acid solvated solvent systems at 303 K: (a) TBP/\( n \)-DD (b) TAP/\( n \)-DD and (c) T2MBP/\( n \)-DD.
The dynamic viscosity of TBP exhibit a distinct curvilinear trend in the temperature range 208.15–338.15 K, whereas the data could be approximated by a linear equation in the temperature range 267.15–338.15 K. In the present study, ln viscosity vs 1/T data were plotted for water as well as acid solvated 1.1 M TalP/n-DD systems (Figures 10 and 11) and fitted using Andrade’s Equation (4).
Table 2. Physicochemical parameters of unirradiated, 500 kGy irradiated and alkali washed (1 contact) 1.1 M TalP/n-DD solution at 303 K.

| 1.1 M TalP/n-DD (water saturated) | Before irradiation | After irradiation (500 kGy) | After NaOH wash |
|-----------------------------------|--------------------|-----------------------------|-----------------|
|                                   | Density (g/mL)    | Viscosity (mPa.s) | IFT (mN/m) | Density (g/mL) | Viscosity (mPa.s) | IFT (mN/m) | Density (g/mL) | Viscosity (mPa.s) | IFT (mN/m) |
| TBP                               | 0.809             | 1.54            | 6.8        | 0.812         | 1.80            | 5.2        | 0.810         | 1.72            | 5.4        |
| TAP                               | 0.814             | 1.88            | 17.1       | 0.816         | 2.06            | 10.7       | 0.815         | 2.00            | 11.5       |
| T2MBP                             | 0.812             | 1.74            | 11.6       | 0.817         | 2.07            | 6.8        | 0.815         | 2.01            | 7.2        |

\[
\ln \eta = A + \left(\frac{B}{T}\right) \tag{4}
\]

where, \(\eta\) is the viscosity in mPa.s, T is the temperature in K, \(A = \ln(N_0h/V)\) and \(B = (-\Delta G^*/R)\) are Andrade’s coefficients. The Andrade’s constants A and B were obtained from the plot for both the systems and the Gibbs energy change of activation \(\Delta G^*\) in kJ/mol was deduced (Tables 3 and 4). It can be observed from Table 3 that among the various water saturated systems, the magnitude of Andrade’s coefficients and \(\Delta G^*\) is highest for TAP and least for TBP in n-DD. A comparative analysis of the data obtained from the Andrade’s equation for various unirradiated and gamma irradiated acid solvated solvents (Table 4) show that there is an increase in the magnitude of A, B and \(\Delta G^*\) with the increase in gamma irradiation dose from 0 to 1000 kGy for TalP systems. The higher value of \(\Delta G^*\) upon irradiation implies that there exists a large energy barrier for initiating the flow process that might be due to the formation of various degradation products having high degree of association or intermolecular forces acting between them.

**Interfacial activity of water solvated TBP, TAP and T2MBP in n-DD systems**

The interfacial activity of TBP/n-DD•H\(_2\)O, TAP/n-DD•H\(_2\)O and T2MBP/n-DD•H\(_2\)O has been comparatively analysed using the Szyszkowski adsorption isotherm given by equation (5)[58]

\[
y_i = y_0 \left[1 - B_{SZ} \ln\left(\frac{c}{A_{SZ}} + 1\right)\right]; \quad 0 < c < 0.1 \text{ M} \tag{5}
\]

where, \(y_i\) is the IFT of a given system at a particular extractant concentration (c), \(y_0\) is the IFT of the extractant free system (c = 0), \(A_{SZ}\) and \(B_{SZ}\) are Szyszkowski adsorption coefficients. The coefficients for water saturated TBP, TAP and T2MBP systems have been estimated by least square fitting of the IFT data (against water) as a function of extractant concentration (less than 10\(^{-1}\) M) to equation (5) as shown in Figure 12. A good fit has been obtained for all the three systems with \(R^2\) value greater than 0.99. The parameters, maximum surface excess (\(\Gamma_{\infty}\)), the minimum interfacial area (\(A_{\min}\)
Figure 10. Andrade’s plot of variation of viscosity as a function of temperature for water saturated 1.1 M TalP/n-DD systems.

Figure 11. Andrade’s plot of variation of viscosity as a function of temperature for acid solvated 1.1 M TalP/n-DD with and without gamma irradiation: (a) TBP/n-DD (b) TAP/n-DD and (c) T2MBP/n-DD systems.
Table 3. Constants of Andrade’s equation for various water saturated TalP/n-DD solvents in the temperature range 298.15 to 323.15 K.

| 1.1 M TalP/n-DD•H₂O   | A      | B      | ΔG° (kJ/mol) |
|------------------------|--------|--------|--------------|
| TBP                    | −5.16  | 1.69x10⁻³ | −14.07       |
| TAP                    | −5.90  | 2.00x10⁻³ | −16.54       |
| T2MBP                  | −5.31  | 1.78x10⁻³ | −14.79       |

Table 4. Constants of Andrade’s equation for various acid solvated TalP/n-DD solvents in the temperature range 298.15 to 323.15 K.

| Condition         | 1.1 M TalP/n-DD•HNO₃ |
|-------------------|----------------------|
|                   | A            | B (x10⁻³) | ΔG° (kJ/mol) |
|                   | TBP          | A            | B (x10⁻³) | ΔG° (kJ/mol) |
|                   | TAP          | A            | B (x10⁻³) | ΔG° (kJ/mol) |
|                   | TAP          | A            | B (x10⁻³) | ΔG° (kJ/mol) |
| Unirradiated      | −4.36        | 1.50        | −12.46     | −5.10        | 1.75        | −14.55     |
| 100 kGy irradiated| −4.93        | 1.68        | −13.93     | −5.04        | 1.74        | −14.44     | −5.15        | 1.78        | −14.77     |
| 500 kGy irradiated| −5.14        | 1.76        | −14.62     | −5.11        | 1.78        | −14.84     | −5.29        | 1.84        | −15.30     |
| 1000 kGy irradiated| −5.21       | 1.82        | −15.11     | −5.59        | 1.98        | −16.47     | −5.87        | 2.05        | −17.04     |

Figure 12. Szyszkowski’s isotherm least square fitting for water solvated (a) TBP, (b) TAP and (c) T2MBP systems in n-DD at 303 K.
occupied by a statistical molecule in the absorbed layer and the free energy of adsorption \((-\Delta G_{\text{ad}})\) are computed by the Equations (6)–(8), respectively, and provided in Table 5.

\[
\Gamma_\infty = \frac{B_{SZ} \gamma_0}{RT} \tag{6}
\]

\[
A_{\text{min}} = \frac{1}{N_A \Gamma_\infty} \tag{7}
\]

\[
\Delta G_{\text{ad}} = -RT \ln(A_{SZ}) \tag{8}
\]

In can be seen from Table 5 that the different TalP having comparable extraction behaviour also have similar values of free energy of adsorption. However, among TBP, TAP and T2MBP, as expected, TBP with a lower molar mass is found to have lower \(A_{\text{min}}\) value. This results in a higher value for the excess concentration of extractant at the interface than in bulk (\(\Gamma_\infty\)) which is in turn responsible for the slightly higher magnitude of \(\Delta G_{\text{ad}}\). The higher \(\Delta G_{\text{ad}}\) is also in correlation with the lower IFT value observed for TBP-based systems.

Overall, a summary of certain important properties of TBP, TAP and T2MBP obtained in the present study and from the earlier reports during the solvent extraction process of spent fuel reprocessing is compiled in Table 6.

### Conclusion

In the present work, the hydrodynamic behaviour (density, viscosity and IFT) of three trialkyl phosphate solvent systems viz. TBP, TAP and T2MBP has been analyzed in detail. The effects of the extractant concentration and gamma irradiation dose on the physicochemical properties have been determined. The viscosity and IFT values of TAP and T2MBP-based systems were observed to be marginally higher in comparison with that of TBP. Higher IFT value would be responsible for faster phase separation during the solvent extraction process. It has been seen that there was a transformation in the properties of TalPs samples upon irradiation and the trend was found to be similar for all the three solvent systems. This variation is because of the presence of several degradation products originated from the diluent and extractants in the case of irradiated solvents. The Gibbs energy change of activation and interfacial activity of the systems have studied using Andrade’s equation and Szyszkowski adsorption

**Table 5.** Szyszkowski’s adsorption isotherm for water saturated TalP/n-DD solvents at 303 K.

| System  | \(A_{\text{iz}}\) \times 10^{-4} \text{ mol dm}^{-3} | \(B_{\text{iz}}\) \times 10^{-2} | \(\Gamma_\infty\) \times 10^{-6} \text{ mol m}^{-2} | \(A_{\text{min}}\) \times 10^{-18} \text{ m}^{2} | \(-\Delta G_{\text{ad}}\) (kJ mol\(^{-1}\)) |
|---------|---------------------------------|-----------------|------------------|-----------------|------------------|
| TBP     | 1.72                            | 9.03            | 1.88             | 0.88            | 21.84            |
| TAP     | 2.00                            | 8.56            | 1.78             | 0.93            | 21.46            |
| T2MBP   | 2.01                            | 8.07            | 1.68             | 0.99            | 21.44            |
**Table 6.** Comparison of the Properties of TBP, TAP and T2MBP.

| Property                              | TBP     | TAP     | T2MBP   |
|---------------------------------------|---------|---------|---------|
| Molecular structure                   | ![Molecular structure](image1) | ![Molecular structure](image2) | ![Molecular structure](image3) |
| For neat compounds                    |         |         |         |
| Solubility of TaIP in H₂O (mg/L) at 299 K (±3%)[^35] | 388     | 19      | 24      |
| Solubility of H₂O in TaIP (mol/L) at 299 K (±3%)[^35] | 3.72    | 2.26    | 2.18    |
| Thermal degradation onset (K) (±0.1 K)[^40] | 527     | 539     | 521     |
| For 1.1 M TaIP/n-DD                   |         |         |         |
| Density of water saturated TaIP (g/mL) at 299 K (±0.2%) | 0.809   | 0.814   | 0.812   |
| Viscosity of water saturated TaIP (mPa.s) at 303 K (±0.2%) | 1.54    | 1.88    | 1.74    |
| IFT against 4 M HNO₃ (mN/m) at 303 K (±0.1 mN/m) | 15.3    | 18.5    | 19.2    |
| Thermal degradation onset (K) (±0.1 K)[^40] | 509     | 535     | 535     |
| Th(IV) third phase limit at near zero free acid (mol/L) 303 K (±1%)[^59] | 0.223   | 0.366   | 0.374   |
| Pu(IV) third phase limit at 4 M HNO₃ (mol/L) 303 K (±1%) | 0.225[^60] | No third phase formation | No third phase formation |
| Zr(IV) third phase limit at 5 M HNO₃ (mol/L) 303 K (±1%)[^49] | 0.099   | 0.160   | 0.229   |
isotherm, respectively. The viscosity, IFT and density values of 1.1 M T2MBP/\(n\)-DD were found to be within the range, which is required in order to be acceptable for solvent extraction processes. In addition to the lower third-phase formation behaviour with tetravalent metal ions as well as lower aqueous solubility of T2MBP, the performance of this extractant in connection with its employment in the reprocessing of spent fuel is suitable for plant operations from the hydrodynamic point of view also.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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