

TODGA-DOHyA: Physicochemical Insights into a Stable Solvent System for Nuclear Reprocessing

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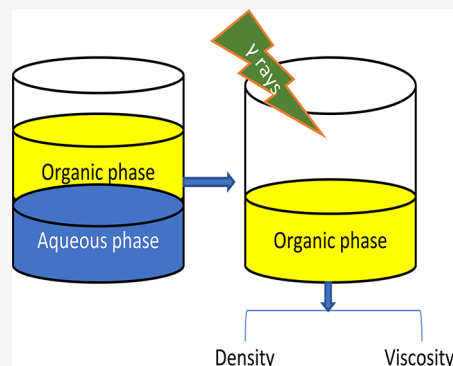


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ABSTRACT: *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), in *n*-dodecane, effectively separates trivalent metal ions but triggers early third-phase formation in the presence of higher metal ion concentrations from nitric acid. To mitigate this, *N,N*-dioctyl-2-hydroxyacetamide (DOHyA), a phase modifier for TODGA, forms a combined solvent system composed of TODGA+DOHyA/*n*-DD (*n*-DD = *n*-dodecane), which efficiently separates trivalent metal ions from radioactive waste. However, understanding the physicochemical behavior and radiolytic stability of this solvent before industrial-scale application is crucial. Hence, this study investigates the density and viscosity of TODGA+DOHyA/*n*-DD and the results obtained were compared with the individual systems. The results revealed a decrease in viscosity and density with increasing temperatures at all doses, and the solvents follow the trend as 0.15 mol kg^{−1} of TODGA + 0.29 mol kg^{−1} of DOHyA/*n*-DD > TODGA/*n*-DD > DOHyA/*n*-DD. In addition, although the density and viscosity increases with the gamma dose in all systems, TODGA + DOHyA/*n*-DD displays minimal change, signifying exceptional stability under irradiation. Thermodynamic parameters revealed weak molecular interactions in TODGA + DOHyA/*n*-DD. In summary, this study highlights the stability of TODGA + DOHyA/*n*-DD, with minor density and viscosity changes under irradiation, spotlighting its potential for nuclear reprocessing.



1. INTRODUCTION

The partitioning of long-lived trivalent metal ions such as lanthanides and actinides from high-level liquid waste (HLLW) followed by their transmutation into stable or short-lived radio-nuclides has been envisaged worldwide for the proper management of nuclear waste.^{1–5} Several approaches have been proposed and demonstrated for the efficient separation of trivalent actinides from HLLW.^{6–9} Currently, the separation of trivalent metal ions is carried out through a complex two-step procedure, which involves the separation of lanthanides and actinides in the first step, followed by their mutual separation in the second step. It is worth to note that in the quest to separate minor actinides, several research studies are still progressing. For instance, the EXAm process introduces an innovative approach where americium and lighter lanthanides are coextracted initially, with the subsequent selective removal of americium in the second stage.^{8,9}

However, it is essential to separate the trivalent metal ions from the HLLW. In view of this, diglycolamides (DGAs), a class of extractants, were studied extensively and were found to be suitable candidates for the partitioning of trivalent metal ions from HLLW.^{1–5} Among these, *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) in a nonpolar diluent, *n*-dodecane (*n*-DD), was considered as a promising system for the partitioning

of trivalent f-ions from the HLLW.^{3,10,11} However, it has certain limitations such as early third-phase formation when contacted with higher concentrations of nitric acid and/or trivalent metal ions from nitric acid. In this view, several researchers have proposed various methods to prevent third-phase formation during the solvent extraction procedure.^{7,12–16} The addition of phase modifiers to the extractant system has been found to be one of the effective options for the prevention of third-phase formation.^{12–16} *N,N*-dioctyl hydroxyl acetamide (DOHyA) serves as a good phase modifier for the TODGA/*n*-DD system during the extraction of trivalent metal ions from HLLW via solvent extraction procedure.^{16–20} The structures of TODGA and DOHyA are shown in Figure 1.

Prathibha *et al.* reported that DOHyA, a radiolytically degraded product of TODGA, can also take part in the extraction of trivalent metal ions from nitric acid medium along with TODGA during the solvent extraction.^{17,18} In view of this, previously we investigated the extraction behavior of

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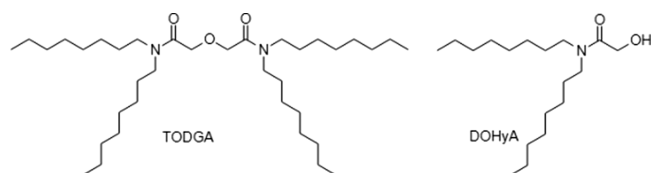


Figure 1. Chemical structures of TODGA and DOHyA.

solvent systems, viz, DOHyA/*n*-DD, TODGA/*n*-DD, and TODGA + DOHyA/*n*-DD toward nitric acid and Nd(III) from nitric acid and found that the extraction follows the order TODGA > TODGA + DOHyA > DOHyA in *n*-DD medium,^{19,20} thus revealing the promising nature of the combined solvent system for the separation of trivalent actinides from HLLW.^{19,20} However, there is a need to investigate the physico-chemical behavior and radiolytic stability of this solvent system before industrial-scale applications. Hence, this study explores the physicochemical properties, particularly density and viscosity, of the combined solvent system composed of 0.15 mol kg⁻¹ of TODGA and 0.29 mol kg⁻¹ of DOHyA in *n*-DD medium.

Moreover, the development of solvent extraction equipment for the large-scale separation of trivalent metal ions from aqueous solution requires precise estimation of viscosity and density of the solvent system.^{21–26} The density of the solvent determines the rate of mass transfer, whereas the viscosity of the solvent determines the flow of liquids.²⁶ These physical properties of the solvent are likely to be affected upon radiolysis, which may affect the performance of the solvent systems toward the separation of metal ions.^{27–31} Hence the stability of the solvent system toward radiation is one of the important property to be investigated to be employed for the separation of minor trivalent actinides from high active nuclear waste. Extensive studies on the solvent extraction and third-phase formation behavior of 0.15 mol kg⁻¹ of TODGA and 0.29 mol kg⁻¹ of DOHyA in *n*-DD toward trivalent metal ions is already reported.^{19,20} However, the physico-chemical properties and their variation as a function of the absorbed dose are limited in the literature. Hence, the aim of the present investigation is to determine the physico-chemical behavior of the combined solvent system (0.15 mol kg⁻¹ of TODGA and 0.29 mol kg⁻¹ of DOHyA in *n*-DD) at various temperatures and absorbed gamma doses. In addition, important properties such as the activation energy of viscous flow, the molar volume, the molar excess volume, excess viscosity, and other thermodynamic functions were computed in order to understand the intermolecular interactions in the solvent systems.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Analytical grade chemicals or solvents with purity > 98% were utilized in this work without further purification. TODGA was purchased from M/s Orion Chemical Company, Mumbai, India and was further purified by a column chromatographic procedure mentioned elsewhere.^{32,33} DOHyA was synthesized and purified by the procedure outlined elsewhere.^{17,19,20} The ¹H NMR and FTIR spectra recorded for identification is provided as [Spectrum S1](#) in the Supporting Information. The weighed amounts of DOHyA or TODGA were mixed in *n*-DD (Alfa Aesar, 99%, viscosity: 0.00134 Pa s, refractive index: 1.421) solution to make solutions of desired compositions. Nitric acid concentration in the stock solution was estimated by conventional

acid–base titration using phenolphthalein as the indicator to detect the end point. The stock solution of Nd(III) was made by weighing a known amount of Nd(NO₃)₃·6H₂O and dissolving it in dilute nitric acid solution. The mixing of the aqueous and organic phases during the extraction studies was carried out in a vertical tube vibrating rotator for 30 min. Complexometric EDTA titration was used to estimate the concentration of Nd(III) in the aqueous and organic phases (obtained during extraction) using methyl thymol blue as the indicator. The concentration of nitric acid in both aqueous and organic phases after the extraction was measured by employing standard acid–base titration. Saturated potassium oxalate solution was added as a masking agent for Nd(III) to determine the free acidity. The detailed list of chemicals employed in the present study is tabulated in [Table 1](#).

Table 1. List of Chemicals Employed in This Study

Compound	Structures	CAS number	Supplier	Molecular weight	Purity
Tetraoctyl-3-oxapentane diamide (TODGA) (Column chromatography method for purification)		342794-43-8	M/s Orion Chemical Company, Mumbai, India	580.97	>98%
Dioctyl hydroxylacetamide (DOHyA)		Synthesised and purified by column chromatographic procedure*, Characterised by ¹ H NMR and ATR-FTIR techniques (spectrum S1)			>98%
<i>n</i> -dodecane		112-40-3	Alfa Aesar	170.33	>99 %
Nitric acid	HNO ₃	7697-37-2	Sigma-Aldrich	63.01	>70%
Neodymium(III) nitrate hexahydrate	Nd(NO ₃) ₃ ·6H ₂ O	16454-60-7	Sigma-Aldrich	438.35	> 99.9 %
Ethylene diaminetetraacetic acid		60-00-4	Sigma-Aldrich	292.24	≥99.0%
Methyl thymol blue sodium salt	C ₂₇ H ₄₀ N ₂ Na ₄ O ₁₃ S	1945-77-3	Sigma-Aldrich	844.74	95%
Potassium oxalate monohydrate		6487-48-5	Sigma-Aldrich	184.23	99%
Hexamethylenetetramine		100-97-0	Sigma-Aldrich	140.19	≥99.0%
Sodium hydroxide	NaOH	1310-73-2	Sigma-Aldrich	40.00	99.99%
Phenolphthalein		77-09-8	Sigma-Aldrich	318.32	99%

*Column chromatography over silica gel using 30 vol % ethyl acetate in petroleum ether as the eluent.

2.2. Thermophysical Property Measurements. The density and viscosity of all samples were assessed as per ASTM-D4052 using an Anton Paar DMA 4500 digital vibrating U-tube densitometer with automated viscosity correction in the range of temperatures between 298 and 323 K. The standard uncertainties associated with density measurements were estimated to be less than 0.005 kg m⁻³. The apparatus was calibrated daily using ambient air ($\rho = 1.1839$ kg m⁻³ and $\eta = 1.86 \times 10^{-5}$ Pa s) and Millipore quality water ($\rho = 997.043$ kg m⁻³ and $\eta = 0.89 \times 10^{-3}$ Pa s) at 298 K under the pressure of 0.1 MPa. The dynamic viscosity of each

sample was measured using a Hoeppler's principle-based Lovis 2000 ME Anton Paar viscometer.^{23,24} The standard uncertainties associated with the viscosity measurements were estimated to be less than 0.05 Pa s. For the density measurements, approximately 3 mL of sample was utilized, whereas for the viscosity measurements, 1 mL of sample was adequate to fill the tube. Prior to the experiment, the tube was cleaned with acetone, and the viscosity value was adjusted to that of dry air. The instrument was calibrated using the standard provided by Anton Paar Co., Austria. The measurement range of viscosity was from 0.3×10^{-3} to 6.5×10^{-2} Pa s using the rolling ball technique. The temperature was controlled by a built-in precise Peltier thermostat with an uncertainty of 0.02 K. At least five measurements were done, and the average result was mentioned in the manuscript.

2.3. Dynamic Light Scattering. Dynamic light scattering (DLS) analysis was carried out using a Malvern Zetasizer device (UK, Model: Nano ZS 90). The fundamental principle behind this technique involves the Brownian motion exhibited by molecules in a solution. When a beam of monochromatic light is directed into a solution containing randomly moving molecules, they undergo scattering in all directions which leads to random fluctuations in the intensity of the scattered light at a particular angle with respect to time. These temporal fluctuations are fed into an autocorrelator which gives information on the diffusion coefficient (D) of aggregates. The Stokes–Einstein relation equating the translational diffusion coefficient D and hydrodynamic diameter (d_h) can be used for calculating the aggregate size as demonstrated in eq 1.

$$d_h = \frac{k_B T}{3\pi\eta D} \quad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the dispersion medium.

Approximately, 0.5 mL of the organic phase was placed in a 3 mm quartz cuvette and fixed in the cuvette cell. To ensure a dust-free sample, the material was filtered through a 0.3 μ m disposable polypropylene membrane filter before DLS measurements. A monochromatic He–Ne laser with a wavelength 632.8 nm (4 mW) was illuminated on the sample, and the intensity of scattered light at a right angle to the incident beam was recorded at 298 K to determine the size of reverse micellar aggregates. In this case, the viscosity and refractive index value of the dispersion medium (n -DD) were taken as 1.34×10^{-3} Pa s and 1.421, respectively, for all samples. DLS measurements were repeated a minimum of 10 times for each sample, to assess data reproducibility with a relative standard uncertainty, $U_r = 0.05$. The particle size derived from these measurements was validated by employing standard polystyrene latex particles dispersed in an aqueous solution, providing an average particle size of 60 nm. Furthermore, the polydispersive index (PDI) in DLS studies gives an idea on the width of the aggregate distribution in the solution. A PDI of 0.2 or less indicates that the sample is monodisperse, and a PDI more than 0.7 is not suitable for the DLS analysis. In the present study, the PDI determined for all measurements was found to be <0.2. Therefore, the aggregate distribution obtained in the present study is regarded as monodisperse.¹⁹

2.4. Irradiation Studies. The organic solution made up of either 0.15 mol kg⁻¹ of TODGA or 0.29 mol kg⁻¹ of DOHyA

or 0.15 mol kg⁻¹ of TODGA and 0.29 mol kg⁻¹ of DOHyA in n -DD was exposed to various γ radiation levels using a ⁶⁰Co γ -chamber facility with a dosage rate of 1.7 kGy h⁻¹. The dose rate of the γ -chamber was calibrated using the Fricke dosimetric technique.³⁴ The organic sample was collected in a glass test tube with a stopper and positioned statically in an irradiation chamber facility.^{22–24,38} The samples were exposed to radiation at varied absorbed dose levels, and at predetermined intervals, the physico-chemical properties of the radiation-exposed samples were measured.

2.5. Sample Preparation. Case 1: Equal amounts (in mL) of organic phase composed of 0.15 mol kg⁻¹ of TODGA and 0.29 mol kg⁻¹ of DOHyA in n -DD and an aqueous phase made up of different concentrations of nitric acid or Nd(III) in nitric acid were equilibrated for an hour at 298 K. After equilibration, the organic phase alone was subjected to density and viscosity measurements.

Case 2: Equal amounts (in mL) of aqueous phase [nitric acid or nitric acid with Nd(III) of different concentrations] and organic phase composed of 0.15 mol kg⁻¹ of TODGA and 0.29 mol kg⁻¹ of DOHyA in n -DD were equilibrated for an hour at room temperature (298 K). After equilibration, the organic phase alone was exposed to various absorbed gamma doses, and the density and viscosity of the irradiated samples were measured.

3. RESULTS AND DISCUSSION

3.1. Density and Viscosity Measurements. Understanding the solvent extraction process requires an in-depth idea about the interactions of molecules in the solvent phase and the evaluation of the physicochemical properties such as density and viscosity, which offer more insights into these molecular interactions.^{35,36} Typically, the organic phase has a lower density than the aqueous phase, and this density difference must be sufficient for the quicker phase disengagement during solvent extraction. Another parameter that measures how easily liquids flow and how easily solutes diffuse in organic phases is viscosity. It is crucial to ascertain these characteristics of the combined solvent system under the circumstances present throughout the solvent extraction process.

3.1.1. Density of Individual and Combined Solvent Systems. Table 2 illustrates the variation in density of neat

Table 2. Variation in the Density Measurement of TODGA and DOHyA (Neat) as a Function of Temperature at 0.1 MPa of Pressure^a

organic phase	density/kg m ⁻³					
	298 K	303 K	308 K	313 K	318 K	323 K
DOHyA	902	899	895	892	888	885
TODGA	905	902	898	895	891	888

^aStandard uncertainties u are $u(\rho) = 0.5$ kg m⁻³, $u(T) = 0.01$ K, and $u(P) = 10$ kPa.

TODGA and DOHyA as a function of various temperatures. When the temperature is raised from 298 to 323 K, it was found that the density of neat TODGA reduces from 905 to 888 kg m⁻³ and that of DOHyA decreases from 902 to 885 kg m⁻³. The more number of alkyl chains present in the TODGA molecule compared to the DOHyA molecule may account for the higher density of TODGA. Since the densities of TODGA and DOHyA are similar to those of the aqueous phase (1100

kg m⁻³), a paraffinic diluent (*n*-dodecane in this instance) is required to increase the disparity between the densities of both (aqueous and organic) phases.

Table 3 shows the density variation in 0.15 mol kg⁻¹ of TODGA in *n*-DD, 0.29 mol kg⁻¹ of DOHyA in *n*-DD, and

Table 3. Density Variations in 0.15 mol kg⁻¹ of TODGA in *n*-DD, 0.29 mol kg⁻¹ of DOHyA in *n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA in *n*-DD as a Function of Temperatures at a Pressure of 0.1 MPa^a

temperature/K	density/kg m ⁻³		
	0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD
298	759	754	767
303	755	750	763
308	751	747	760
313	748	743	756
318	744	739	752
323	740	736	749

^aStandard uncertainties are $u(T) = 0.02$ K, $u(\rho) = 2$ kg m⁻³, $u(P) = 0.50$ kPa, and $u(m) = 0.02$ mol kg⁻¹. 'm' represents molality.

0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA in *n*-DD as a function of various temperatures. Upon addition of *n*-DD (density of *n*-DD = 750 kg m⁻³), it was found that the densities of all systems dropped, with the difference between the densities of the organic and aqueous phases being around 250 kg m⁻³, and this density difference was adequate for the liquid–liquid extraction without any phase disengagement in the present study. Therefore, the organic solution in *n*-DD was considered suitable for effective mixing and quicker phase disengagement of two phases during the solvent extraction procedure. In addition, it was also found that density and viscosity of the solvent systems increase with the increase of temperature. Jammu *et al.* reported that the density of neat TODGA varied from 904.34 to 877.71 kg m⁻³ when temperature was increased from 298 to 323 K under unirradiated condition, which is in good agreement with the present data with a standard uncertainty of 0.8 kg m⁻³.²³

3.1.2. Density Variation in Organic Phase with Nitric Acid Extraction. During the liquid–liquid extraction procedure, the organic phase comes into contact with a target metal ion and the nitric acid-containing aqueous phase. The metal ions and nitric acid extraction into the less dense organic phase during the solvent extraction procedure may likely affect the density of the organic phase. In view of this, it is important to understand how the density of the organic phase varies with the extraction of nitric acid. The solvent systems of desired compositions, (0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of DOHyA/*n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD), were contacted with nitric acid solutions of various concentrations ranging from 1.05 to 11.33 mol kg⁻¹, and the density of the acid-extracted organic phase was measured. The results obtained are shown in Table 4. It is clear that the density of TODGA/*n*-DD, DOHyA/*n*-DD and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD increased with the increase in the initial concentration of nitric acid in the aqueous phase, which can be attributed to the increase in the extraction of water and nitric acid into the organic phase. The nitric acid extraction behavior of 0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of DOHyA/*n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD are shown in Table 5. It can be seen that the amount of nitric acid extracted to the organic phase increases as a function of the initial nitric acid concentration in all cases with LOC (limiting organic phase concentration) values being different as shown in Table 5. This increase in the extraction of nitric acid into the organic phase increases the density of the organic phase (organic phase loaded with nitric acid) (Table 4). It was also found that the density of the acid-equilibrated organic phase follows the order: 0.29 mol kg⁻¹ of DOHyA/*n*-DD < 0.15 mol kg⁻¹ of TODGA/*n*-DD < 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD. Moreover, with increasing temperature, decreasing trends in densities were observed for all systems.

3.1.3. Density of Combined Solvent System as a Function of Extractant Composition. Table 6 depicts the density variation in the combined solvent system in *n*-DD of various compositions, including 0.137 mol kg⁻¹ of TODGA + 0.137 mol kg⁻¹ of DOHyA, 0.142 mol kg⁻¹ of TODGA + 0.442 mol

Table 4. Variation in the Density of Nitric Acid-Loaded Organic Phases as a Function of Temperature at a Pressure of 0.1 MPa^{a,b}

organic phase	initial HNO ₃ /mol kg ⁻¹	density/kg m ⁻³					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	Organic phase alone	759	755	751	748	744	740
	1.05	760	756	752	749	746	741
	4.72	766	763	759	755	751	748
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	754	750	747	743	739	736
	1.05	754	751	747	744	740	736
	4.72	756	753	749	745	742	738
	11.33	761	757	753	747	745	742
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	767	763	759	756	752	749
	1.05	768	765	761	758	754	750
	4.72	773	769	765	762	758	754
	11.33	775	771	767	763	759	756

^aPrior to density measurements, the organic phase was equilibrated with nitric acid. Organic phase: TODGA/*n*-DD or DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: 1.05–11.33 mol kg⁻¹ HNO₃; aqueous to organic phase volume ratio: 1:1.

^bStandard uncertainties are $u(T) = 0.01$ K, $u(\rho) = 1$ kg m⁻³, $u(P) = 0.50$ kPa, $u(m_a) = 0.02$ mol kg⁻¹, and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

Table 5. Extraction Behavior of Nitric Acid into the Organic Phases as a Function of the Initial Nitric Acid Concentration in Aqueous Phase at 298 K^{a,b,c}

initial $\text{HNO}_3/\text{mol kg}^{-1}$	HNO_3 in TODGA/ <i>n</i> -DD/ mol kg^{-1}	HNO_3 in DOHyA/ <i>n</i> -DD/ mol kg^{-1}	HNO_3 in combined solvent system in <i>n</i> -DD/ mol kg^{-1}
Neat (Organic phase alone)	No extraction of nitric acid or water	No extraction of nitric acid or water	No extraction of nitric acid or water
1.05	0.036	0.013	0.064
2.17	0.093	0.016	0.131
3.40	0.117	0.031	0.197
4.72	0.187	0.057	0.276
6.17	0.235	0.094	0.357
7.77	0.243 (LOC)	0.159	0.438
11.33		0.213	0.506
15.70		0.266 (LOC)	0.612 (LOC)

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: 1.05–11.33 mol kg⁻¹ HNO₃; aqueous to organic phase volume ratio: 1:1. ^bLOC- Limiting organic phase concentration. ^cStandard uncertainties are $u(m_a) = 0.03 \text{ mol kg}^{-1}$, and $u(m_b) = 0.03 \text{ mol kg}^{-1}$, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

kg⁻¹ of DOHyA, and 0.068 mol kg⁻¹ of TODGA + 0.137 mol kg⁻¹ of DOHyA in *n*-DD. The organic phase was equilibrated with nitric acid of varying concentrations. The acid-extracted organic phases were subjected to density measurements. It is obvious that the composition with 0.137 mol kg⁻¹ of TODGA and 0.442 mol kg⁻¹ of DOHyA in *n*-DD showed a higher density compared to other compositions. The density of the combined solvent system was found to increase with an increase in the initial nitric acid concentration and also found to decrease as a function of temperature. The greater extraction of nitric acid, which is unavoidably followed by water extraction, is what causes the increase in density with an increase in the initial nitric acid concentration.

3.1.4. Density Variation in Organic Phase upon Nd(III) Extraction. Density variation in the organic phase after the extraction of Nd(III) metal ions of various concentrations from 4.72 mol kg⁻¹ of nitric acid at different temperatures is shown in Table 7. The splitting of organic phase termed as third-phase formation, was observed when 4.72 mol kg⁻¹ of nitric acid containing Nd(III) above 0.0063 mol kg⁻¹ [1 g/L Nd(III)] was added to the organic solution of TODGA/*n*-DD of composition 0.15 mol kg⁻¹, as shown in Table 7. Therefore, the densities of Nd(III)-extracted TODGA/*n*-DD (0.15 mol kg⁻¹) phase could not be detected beyond 0.0063 mol kg⁻¹ of Nd(III) in the aqueous phase. Table 7 also shows the variation in density of 0.29 mol kg⁻¹ of DOHyA/*n*-DD and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD as a function of Nd(III) in 4.72 mol kg⁻¹ of HNO₃. It is evident that when the Nd(III) concentration in 4.72 mol kg⁻¹ of nitric acid increases, the density of the organic phase also increases (Table S1). This can be attributed to the extraction of Nd(III) into the organic phase, as discussed elsewhere.^{19,20} The densities of the 0.0063 mol kg⁻¹ Nd(III) extracted organic phase from 1.05 mol kg⁻¹ of nitric acid follows the order 0.29 mol kg⁻¹ of DOHyA/*n*-DD < 0.15 mol kg⁻¹ of TODGA/*n*-DD < 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD. The variation in the densities of each solvent phases as a function of the concentration of Nd(III) in 1.05 mol kg⁻¹ of nitric acid was investigated, and the results are given in Table S2.

3.1.5. Viscosity of Individual and Combined Solvent Systems. Temperature-dependent viscosity measurements were carried out for both individual and combined solvent systems. Prior to the viscosity measurements of the organic solutions in *n*-DD, the viscosity of neat TODGA and DOHyA was measured. The results obtained are plotted in Figure 2 (Table 8). It has been observed that the viscosity of TODGA and DOHyA decreases as the temperature increases. With an increase in temperature from 298 to 323 K, the viscosity of neat TODGA reduces from 0.132 to 0.036 Pa s and that of DOHyA from 0.023 to 0.008 Pa s. Ravi *et al.*²³ and Panja *et al.*³⁷ reports the viscosity and density values of 0.15 mol kg⁻¹ of TODGA/*n*-DD which were found to be in good agreement with our present data. The literature reveals that the viscosity of neat TODGA decreased from 0.091 to 0.0231 Pa s when the temperature is increased from 303.00 to 333.00 K.²³ In addition, the effect of radiation dose on the physicochemical parameters like density and viscosity of 0.15 mol kg⁻¹ of TODGA/*n*-DD was elaborately discussed by Ravi *et al.*, and the results were found to be in good agreement with the present study.²³ Moreover, Pratibha *et al.* has studied the density and viscosity of 0.29 mol kg⁻¹ of DOHyA/*n*-DD which was found to be in good agreement with the values reported in

Table 6. Variation in the Density of the Combined Solvent System in *n*-DD with Temperature at a Pressure of 0.1 MPa at Various Organic Phase Compositions^{a,b}

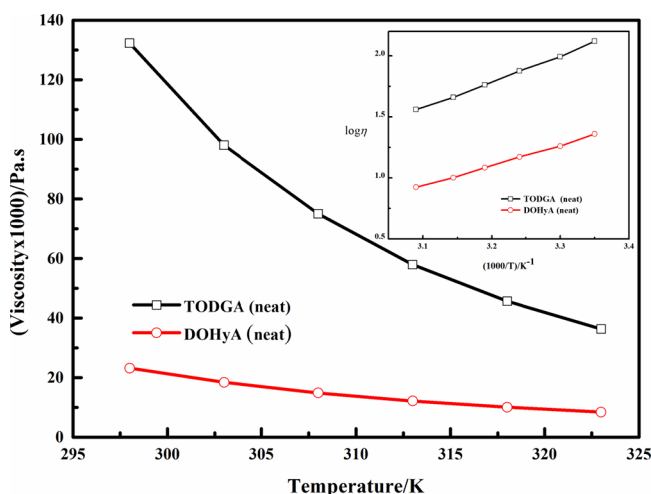
organic phase	initial HNO ₃ /mol kg ⁻¹	density/kg m ⁻³					
		298 K	303 K	308 K	313 K	318 K	323 K
0.05 mol kg ⁻¹ of TODGA + 0.1 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	756	752	748	745	741	737
	1.05	756	753	749	745	742	738
	4.72	759	755	752	748	744	740
0.1 mol kg ⁻¹ of TODGA + 0.3 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	761	757	753	749	746	742
	1.05	766	763	759	756	752	748
	4.72	768	764	760	757	753	749
0.1 mol kg ⁻¹ of TODGA + 0.1 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	761	758	754	751	747	743
	1.05	761	758	754	751	747	743
	4.72	765	762	758	754	751	747

^aPrior to density measurements, the organic phase was equilibrated with the desired nitric acid. Organic phase: 0.137 mol kg⁻¹ of TODGA + 0.137 mol kg⁻¹ of DOHyA, 0.142 mol kg⁻¹ of TODGA + 0.442 mol kg⁻¹ of DOHyA, and 0.068 mol kg⁻¹ of TODGA + 0.137 mol kg⁻¹ of DOHyA in *n*-DD; aqueous phase: 1.05–4.72 mol kg⁻¹ of HNO₃; Aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\rho) = 0.8$ kg m⁻³, $u(P) = 0.50$ kPa, $u(m_a) = 0.02$ mol kg⁻¹, and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

Table 7. Density Variation in the Organic Phase after Extraction of Nd(III) of Various Concentrations from 4.72 mol kg⁻¹ Nitric Acid at Different Temperatures at a Pressure of 0.1 MPa^{a,b}

organic phase	initial Nd(III)/mol kg ⁻¹	density/kg m ⁻³					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	Nitric acid (4.72 mol kg ⁻¹) loaded organic phase	755	752	748	745	741	737
	0.063	766	763	759	755	751	748
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Nitric acid (4.72 mol kg ⁻¹) loaded organic phase	756	753	749	745	742	738
	0.063	758	754	750	747	743	739
	0.019	759	756	752	748	745	741
	0.032	761	758	754	750	747	743
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Nitric acid (4.72 mol kg ⁻¹) loaded organic phase	730	769	765	762	758	754
	0.063	777	773	769	766	762	758
	0.019	781	777	773	769	766	762
	0.032	787	784	779	774	769	764

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: 4.72 mol kg⁻¹ of HNO₃; aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\rho) = 0.7$ kg m⁻³, $u(P) = 0.50$ kPa, $u(m_a) = 0.02$ mol kg⁻¹, and $u(m_b) = 0.03$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

**Figure 2.** Variation in the viscosity of neat TODGA and DOHyA as a function of temperature at a pressure of 0.1 MPa. Inset: Arrhenius-type plot. The standard uncertainty associated with viscosity measurement is 0.05 Pa s and that with temperature, $u(T)$, is 0.02 K.**Table 8.** Viscosity Variation in Neat TODGA and DOHyA as a Function of Temperature at a Pressure of 0.1 MPa^a

organic phase	(viscosity × 1000)/Pa s					
	298 K	303 K	308 K	313 K	318 K	323 K
DOHyA	23.13	18.40	14.84	12.12	10.04	8.40
TODGA	132.30	98.06	75.01	57.91	45.65	36.32

^aStandard uncertainties are $u(T) = 0.01$ K, $u(\eta) = 0.05$ Pa s, and $u(P) = 0.50$ kPa.

the present study.^{17,18} Equation 2 illustrates the Arrhenius-type exponential relation between the liquid's viscosity (η) and temperature.

$$\eta = Ae^{E_a/RT} \quad (2)$$

where R is the universal gas constant, T is the temperature in Kelvin, and E_a and A are the activation energies for the viscous flow and the proportionality constant, respectively.^{24,38,39} The slope of $\log \eta$ vs $1/T$ plot can be used to calculate the activation energy, and the same has been provided as the inset in Figure 2. The activation energies for DOHyA and TODGA

Table 9. Variation in the Viscosity of the 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD Phase as a Function of Temperature at a Pressure of 0.1 MPa^{a,b}

organic phase	initial HNO ₃ /mol kg ⁻¹	(viscosity × 1000)/Pa s					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	Organic phase alone	1.66	1.51	1.38	1.27	1.17	1.05
	1.05	1.68	1.53	1.40	1.27	1.18	1.10
	4.72	1.93	1.72	1.54	1.40	1.28	1.17
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	1.45	1.33	1.22	1.12	1.04	0.97
	1.05	1.49	1.36	1.25	1.14	1.06	0.99
	4.72	1.52	1.38	1.27	1.17	1.05	1.00
	11.33	1.60	1.45	1.31	1.20	1.14	1.03
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	Organic phase alone	1.83	1.66	1.51	1.38	1.27	1.17
	1.05	1.89	1.71	1.56	1.42	1.31	1.20
	4.72	1.98	1.78	1.61	1.47	1.34	1.23
	11.33	2.07	1.84	1.66	1.51	1.38	1.27

^aThe organic phase was equilibrated with nitric acid prior to the viscosity measurements. Organic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; Aqueous phase: 1.05–11.33 mol kg⁻¹ of HNO₃; aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\eta) = 0.02$ Pa s, $u(P) = 0.50$ kPa, $u(m_a) = 0.03$ mol kg⁻¹, and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

Table 10. Aggregate Size Measurements of the Organic Phase after Nitric Acid Extraction at 298 ± 0.02 K^a

	0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD
initial [HNO ₃]/mol kg ⁻¹	aggregate size/nm		
No nitric acid or water extraction	1.99	1.6	2.3
1.05 ± 0.02	2.1	1.6	2.9
2.42 ± 0.01	3.7	1.7	3.7
3.59 ± 0.03	4.9	1.8	4.6
4.72 ± 0.01	7.4	1.9	5.6
7.79 ± 0.02	14.3 ^b	2.3	7.3
11.36 ± 0.02	Beyond which third phase forms	4.48	12.9
15.86 ± 0.01		10.2 ^c	19.8

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: 1.05–15.86 mol kg⁻¹ HNO₃. Aqueous to organic phase volume ratio: 1:1. ^bLAS-limiting aggregate size for the third-phase formation, which is the maximum size limit for the third-phase formation, as discussed elsewhere. ^cStandard uncertainties are $u(m_a) = 0.03$ mol kg⁻¹ and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions. Standard deviation in the aggregate size is ~ ±0.015 nm.

were found to be 32.05×10^3 and 41.15×10^3 J mol⁻¹, respectively. Increased activation energy reported for TODGA molecules indicates stronger intermolecular interactions, possibly due to the polar–polar attractive interactions between the TODGA molecules,²³ which resist the flow of ligands. It is important to note that TODGA has two polar amidic groups, whereas DOHyA has only one amidic moiety (Figure 1). These polar amidic groups are partially responsible for the strong polar–polar interactions which impart higher viscosity values for the TODGA system. In addition, it is naturally expected to have higher viscosity since TODGA possesses a larger molecular size compared to DOHyA molecules. Also, the intramolecular hydrogen bonding which acts in the DOHyA molecule reduces the extent of intermolecular interactions, resulting in a decrease of viscosity. However, due to the greater viscosity of the neat TODGA and DOHyA, it is reasonable to employ diluents like *n*-DD to reduce the viscosity of the resultant solution for reprocessing applications.

3.1.6. Viscosity Variation in Organic Phase upon Nitric Acid Extraction. It is essential to have a thorough understanding of how the viscosity of the organic phase changes with the extraction of nitric acid into the organic phase. The solvent phases, 0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of

DOHyA/*n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD, were contacted with nitric acid solutions of various concentrations ranging from 1.05 to 11.33 mol kg⁻¹, and the acid-extracted organic phases were subjected to viscosity analysis. Since 0.15 mol kg⁻¹ solution of TODGA in *n*-DD forms a third phase at a nitric acid concentration of 7.77 mol kg⁻¹ and above, the nitric acid concentration used for the viscosity measurement study was restricted to 4.72 mol kg⁻¹. Table 9 displays the viscosity of 0.29 mol kg⁻¹ of DOHyA/*n*-DD, 0.15 mol kg⁻¹ of TODGA/*n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD systems upon nitric acid extraction at various temperatures. It was observed that the viscosity of nitric acid-loaded 0.29 mol kg⁻¹ of DOHyA/*n*-DD at all nitric acid concentrations was lower than 0.15 mol kg⁻¹ of TODGA/*n*-DD under similar conditions.

The elevated viscosity in 0.15 mol kg⁻¹ of TODGA/*n*-DD is a result of stronger van der Waals and polar–polar attractive interactions among TODGA molecules, facilitated by a higher number of attached alkyl groups. Since the TODGA molecule has two amidic polar groups and is almost twice as large as DOHyA (Figure 1), the viscosity of 0.15 mol kg⁻¹ of TODGA/*n*-DD is naturally expected to be greater than 0.29

Table 11. Viscosity Variation in the Organic Phase upon Nd(III) Extraction from 1.05 mol kg⁻¹ of Nitric Acid at Different Temperatures at a Pressure of 0.1 MPa^{a,b}

organic phase	initial Nd(III)/mol kg ⁻¹	(viscosity × 1000)/Pa s					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0.006	1.58	1.44	1.32	1.21	1.12	1.04
	0.019	1.50	1.36	1.25	1.15	1.07	0.99
	0.032	1.46	1.34	1.23	1.13	1.05	0.97
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0.063	1.49	1.36	1.25	1.15	1.06	0.99
	0.019	1.49	1.36	1.24	1.14	1.06	0.98
	0.032	1.49	1.36	1.25	1.15	1.06	0.98
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0.063	1.86	1.69	1.54	1.41	1.29	1.19
	0.019	2.15	1.93	1.74	1.59	1.45	1.33
	0.032	2.33	2.08	1.87	1.69	1.54	1.40

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: Nd(III) in HNO₃. Aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.03$ K, $u(\eta) = 0.05$ Pa s, $u(P) = 0.50$ kPa, $u(m_a) = 0.03$ mol kg⁻¹, and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

mol kg⁻¹ of DOHyA/*n*-DD. Typically, the viscosity of the organic phase is reduced by nitric acid and/or water extraction. An increase in the viscosity in all solvent systems was observed upon nitric acid extraction, which can be attributed to the aggregate formation in the organic phase. For instance, the increase in the viscosity of 0.15 mol kg⁻¹ of TODGA/*n*-DD upon nitric acid extraction demonstrates the aggregation of TODGA molecules in the organic phase. Table 10 demonstrates the size of aggregates obtained in TODGA, DOHyA, and combined solvent system in *n*-DD and its distribution in the organic phase. The aggregate size of 0.15 mol kg⁻¹ of TODGA/*n*-DD is determined to be ~2 nm, which is in good agreement with the self-aggregate size of the same system obtained by SAXS and SANS techniques (~2 nm). The distribution of the data into different sizes demonstrates that the chance of self-aggregation is also extremely probable in the case of pure organic phase (0.15 mol kg⁻¹ of TODGA/*n*-DD).⁴⁰

However, the average aggregate size increases as the nitric acid extraction into the organic phase increases, due to the enhanced polar–polar interaction resulting in the formation of bigger reverse micelles in the organic phase.^{19,41} As a result, the 0.15 mol kg⁻¹ of TODGA/*n*-DD phase upon nitric acid loading exhibits a greater viscosity value compared to the organic phase without nitric acid loading. Similar behavior was observed in the case of 0.29 mol kg⁻¹ DOHyA/*n*-DD. Since there is less aggregation in the case of DOHyA/*n*-DD compared to TODGA/*n*-DD (Table 10), the increase in viscosity in this instance is not substantial. The viscosity of 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD was also found to be increased with the increase in the concentration of nitric acid in the aqueous phase. In addition, it is crucial to remember that the third-phase formation limits for 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD and 0.29 mol kg⁻¹ of DOHyA/*n*-DD are higher (>11.33 mol kg⁻¹ nitric acid), which is due to their lesser aggregation tendency. Since their aggregation is less even at higher concentrations of nitric acid, they exhibit less viscosity compared to 0.15 mol kg⁻¹ of TODGA/*n*-DD system.

3.1.7. Viscosity of Organic Phase upon Nd(III) Extraction. Table 11 illustrates the viscosity variation in the individual and combined solvent systems at varying concentrations of Nd(III) from 1.05 mol kg⁻¹ of nitric acid at various temperatures. It can be seen that when the concentration of Nd(III) in 1.05 mol

kg⁻¹ of nitric acid increases, the viscosity of the organic phase also increases. This can be attributed to the increase in the extraction of Nd(III) into the organic phase with the increase in the concentration of Nd(III) in the aqueous phase. The more the extraction of Nd(III) into the organic phase, the more the polar–polar interactions occur, which leads to the enhanced aggregation in the Nd(III)-loaded organic phase.^{23,41} Table 12 displays the aggregate size of organic phase upon

Table 12. Aggregate Size Measurements of the Organic Phase upon Nd(III) Extraction from 1.05 mol kg⁻¹ of Nitric Acid at 298 ± 0.02 K^{a,b}

initial [Nd(III)]/mol kg ⁻¹	0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD
	aggregate size/nm		
Nitric acid (1.05 mol kg ⁻¹)-loaded organic phase	2.1	1.9	2.8
0.006	3.9 ^c	2.1	3.7
0.019		3.2	4.1
0.032		4.3	4.3

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: Nd(III) in HNO₃. Aqueous to organic phase volume ratio: 1:1. The uncertainty associated with the molality is ~ ±0.02 m. Standard deviation in the aggregate size is ~ ±0.02 nm. ^bStandard uncertainties are $u(m_a) = 0.03$ mol kg⁻¹ and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions. Standard deviation in the aggregate size is ~ ±0.02 nm. ^cLAS-limiting aggregate size for the third-phase formation, which is the maximum size limit for the third-phase formation, as discussed elsewhere.⁴¹

Nd(III) extraction from 1.05 mol kg⁻¹ of nitric acid. It is noteworthy that the average aggregate size increases with Nd(III) concentration in the aqueous phase, as described elsewhere.^{19,41} The enhanced aggregation due to the polar–polar interactions leads to an increase in the viscosity of the organic phase as the concentration of Nd(III) in the aqueous phase increases. The variation in the viscosity of 0.29 mol kg⁻¹ of DOHyA/*n*-DD upon Nd(III) extraction is insignificant as the extraction of Nd(III) from 1.05 mol kg⁻¹ of nitric acid into the organic phase is negligible.^{19,20} A similar pattern has been

Table 13. Density Variation in the Organic Phase after Equilibration with 1.05 mol kg⁻¹ of HNO₃ Subjected to Various Radiation Doses with Temperature at a Pressure of 0.1 MPa^{a,b}

organic phase	gamma dose/kGy	density/kg m ⁻³					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0	757	753	750	746	743	739
	100	757	753	750	746	743	739
	250	757	754	750	746	743	739
	500	759	755	752	748	745	741
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	754	751	747	745	740	736
	100	756	753	749	745	742	738
	250	757	753	750	746	742	739
	500	758	755	751	747	744	740
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	768	765	761	758	754	750
	100	765	761	758	754	751	747
	250	766	763	759	756	752	748
	500	767	763	760	756	753	749

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: 1.05 mol kg⁻¹ of HNO₃; aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\rho) = 0.7$ kg m⁻³, $u(P) = 0.50$ kPa, $u(m_a) = 0.02$ mol kg⁻¹, and $u(m_b) = 0.03$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

Table 14. Density Variation in the Organic Phase after Extraction of Nd(III) of Various Concentrations from 1.05 mol kg⁻¹ Nitric Acid at Different Temperatures at a Pressure of 0.1 MPa as a Function of Absorbed Gamma Doses^{a,b}

organic phase contacted with 0.019 mol kg ⁻¹ of Nd(III)	gamma dose/kGy	density/kg m ⁻³					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0	752	748	745	741	737	734
	100	760	757	753	749	745	742
	250	763	759	756	752	748	745
	500	767	764	760	756	753	749
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	754	750	747	743	739	736
	100	756	752	749	745	742	738
	250	757	754	750	746	743	739
	500	758	755	752	748	744	741
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	776	772	768	765	761	757
	100	776	772	768	765	761	757
	250	777	774	770	766	763	759
	500	779	775	772	768	765	761

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: Nd(III) in 1.050 mol kg⁻¹ of HNO₃; aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\rho) = 0.5$ kg m⁻³, $u(P) = 0.50$ kPa, $u(m_a) = 0.03$ mol kg⁻¹, and $u(m_b) = 0.04$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

observed in the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD system. This demonstrates unequivocally that viscosity can be used to investigate the third-phase formation behavior of various solvent systems. Table S4 displays the findings on the variation in the viscosity of Nd(III)-loaded organic phase (from 4.72 mol kg⁻¹ of nitric acid). It was not possible to get the data for 0.15 mol kg⁻¹ of TODGA/*n*-DD as it forms the third phase at these conditions.

3.2. Density and Viscosity of Irradiated Solvents. In order to understand the impact of γ radiation on the physical properties of the solvent system, the organic solutions were exposed to various gamma dosage levels ranging from 0 to 500 kGy. The solvent degrades as a result of the organic phase being exposed to gamma doses, and various degradation products are also formed. The density and viscosity of the organic phase are significantly altered by the presence of these breakdown products. The results thus obtained are illustrated below.

3.2.1. Density of Acid-Loaded Organic Phase at Various Absorbed Dose Levels. Equal volumes of the organic phase made up of 0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of DOHyA/*n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD were equilibrated with 1.05 mol kg⁻¹ of nitric acid. The nitric acid-extracted organic phases were subjected to gamma irradiation to various absorbed dose levels ranging from 100 to 500 kGy. Table 13 displays the variation in the density of solvent systems at various gamma dose levels as a function of temperature. It can be seen that the density of the organic phase does not change significantly upon irradiation; nevertheless, the density of the irradiated solvent phase slightly increases with the absorbed gamma dose at a particular temperature. This might be due to the formation of polar degradation products which resulted from solvent irradiation.^{29–32} Similarly, the organic phases were equilibrated with 4.72 mol kg⁻¹ of nitric acid, and the nitric acid-loaded organic phases were subjected to gamma irradiation. The densities of the gamma-irradiated organic phases were

Table 15. Viscosity Variation in the Organic Phase after Extraction of Nd(III) of Various Concentrations from 1.050 mol kg⁻¹ of Nitric Acid at Different Temperatures at a Pressure of 0.1 MPa at Various Absorbed Gamma Doses^a

organic phase contacted with 1.05 mol kg ⁻¹ of HNO ₃	gamma dose (kGy)	(viscosity × 1000)/Pa s					
		298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0	1.61	1.47	1.32	1.21	1.11	1.02
	100	1.63	1.48	1.34	1.22	1.12	1.03
	250	1.68	1.52	1.39	1.28	1.18	1.09
	500	1.68	1.53	1.40	1.29	1.18	1.09
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	1.49	1.36	1.25	1.18	1.06	0.99
	100	1.56	1.42	1.30	1.24	1.12	1.04
	250	1.59	1.47	1.35	1.29	1.17	1.09
	500	1.66	1.51	1.38	1.27	1.17	1.05
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	1.82	1.65	1.51	1.37	1.26	1.16
	100	1.85	1.67	1.53	1.39	1.28	1.18
	250	1.89	1.71	1.56	1.42	1.31	1.20
	500	1.89	1.71	1.56	1.43	1.31	1.21

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: Nd(III) in 1.050 mol kg⁻¹ of HNO₃; aqueous to organic phase volume ratio: 1:1. Uncertainty associated with viscosity is 2 × 10⁻⁶ Pa s; Uncertainty in temperature is ±0.02 K. The uncertainty associated with molality is ~ ±0.02 mol kg⁻¹.

Table 16. Viscosity Variation in the Organic Phase after Extraction of Nd(III) of Various Concentrations from 4.72 mol kg⁻¹ of Nitric Acid at Different Temperatures at a Pressure of 0.1 MPa at Various Absorbed Gamma Doses^{a,b}

organic phase	initial HNO ₃ /mol kg ⁻¹	gamma dose (kGy)	(viscosity × 1000)/Pa s					
			298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	4.72	0	1.67	1.52	1.39	1.25	1.12	1.02
		100	1.77	1.56	1.43	1.29	1.17	1.06
		250	1.88	1.65	1.49	1.30	1.20	1.11
		500	1.93	1.72	1.54	1.40	1.28	1.17
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	4.72	0	1.49	1.36	1.25	1.18	1.06	0.99
		100	1.56	1.42	1.30	1.24	1.12	1.04
		250	1.56	1.47	1.35	1.29	1.17	1.09
		500	1.66	1.51	1.38	1.27	1.17	1.05
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	4.72	0	1.82	1.65	1.51	1.37	1.26	1.16
		100	1.86	1.68	1.53	1.40	1.28	1.18
		250	1.89	1.71	1.56	1.42	1.31	1.20
		500	1.89	1.71	1.56	1.43	1.31	1.21

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: Nd(III) in 4.72 mol kg⁻¹ of HNO₃. Aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\eta) = 0.07$ Pa s, $u(P) = 0.50$ kPa, $u(m_a) = 0.03$ mol kg⁻¹, and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

determined. The data presented in Tables 13 and S3 are similar.

3.2.2. Density of Nd(III)-Loaded Organic Phase at Various Absorbed Doses. The organic phase made up of either 0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of DOHyA/*n*-DD, or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD were pre-equilibrated with 1.05 mol kg⁻¹ of nitric acid, followed by equilibration with 1.05 mol kg⁻¹ of nitric acid containing 0.019 mol kg⁻¹ of Nd(III) metal ions. The Nd(III)-extracted organic phases were subjected to various gamma doses (0 to 500 kGy), and the density of the irradiated organic phases was assessed at various temperatures. The results thus obtained are presented in Table 14. It is noteworthy that the densities of the irradiated systems are slightly higher than the corresponding unirradiated systems under similar conditions. Moreover, the density of the organic phase was found to increase with the increase in the absorbed dose. However, the densities of all systems were found to decrease as a function of temperature. In a similar manner, the organic phases were contacted with 4.72 mol kg⁻¹ of nitric acid containing Nd(III)

metal ion, and the metal ion-loaded organic phases were subjected to gamma irradiation. The variations in the densities of the organic phases as a function of gamma doses at various temperatures were determined. The results are tabulated in Table S5. At a particular experimental condition, the density of irradiated and unirradiated solvent systems follows the sequence 0.29 mol kg⁻¹ of DOHyA/*n*-DD < 0.15 mol kg⁻¹ of TODGA/*n*-DD < 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD.

3.2.3. Viscosity of Acid-Loaded Organic Phase at Various Absorbed Gamma Dose Levels. The organic phases were contacted with 1.05 mol kg⁻¹ nitric acid, and the acid-extracted organic phases were subjected to gamma irradiation doses ranging from 100 to 500 kGy. The viscosities of the irradiated organic phases were determined, and the results are shown in Table 15 as a function of temperature. The results revealed that the viscosity of the radiation-exposed solvent systems slightly increases with increasing gamma doses and decreases with increasing temperature. However, the viscosity variation

Table 17. Viscosity Variation in the Organic Phase after Extraction of Nd(III) of Various Concentrations from 1.05 mol kg⁻¹ of Nitric Acid at Different Temperatures at a Pressure of 0.1 MPa at Various Absorbed Gamma Doses^{a,b}

		(viscosity × 1000)/Pa s						
organic phase contacted with 0.019 mol kg ⁻¹ of Nd(III) in 1.05 mol kg ⁻¹ of HNO ₃	gamma dose (kGy)	298 K	303 K	308 K	313 K	318 K	323 K	
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	0	1.62	1.49	1.36	1.21	1.10	0.99	
	100	1.66	1.53	1.40	1.31	1.22	1.14	
	250	1.72	1.59	1.46	1.36	1.27	1.20	
	500	1.74	1.60	1.48	1.38	1.29	1.21	
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	1.43	1.31	1.20	1.15	1.01	0.89	
	100	1.55	1.41	1.30	1.20	1.11	1.03	
	250	1.57	1.44	1.33	1.23	1.14	1.06	
	500	1.60	1.49	1.37	1.26	1.16	1.05	
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	0	2.01	1.82	1.59	1.33	1.22	1.10	
	100	2.07	1.87	1.65	1.49	1.35	1.23	
	250	2.10	1.88	1.66	1.51	1.37	1.25	
	500	2.14	1.93	1.75	1.59	1.46	1.34	

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: Nd(III) in 1.05 mol kg⁻¹ of HNO₃; aqueous to organic phase volume ratio: 1:1. ^bStandard uncertainties are $u(T) = 0.02$ K, $u(\eta) = 0.07$ Pa s, $u(P) = 0.50$ kPa, $u(m_a) = 0.03$ mol kg⁻¹, and $u(m_b) = 0.02$ mol kg⁻¹, where m_a represents the molality of organic solvent systems and m_b represents the molality of nitric acid solutions.

Table 18. Variation of Activation Energy of Solvent Phase as a Function of Absorbed Dose Levels^{a,b}

organic phase	activation energy/kJ mol ⁻¹			
	0 kGy	100 kGy	250 kGy	500 kGy
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	13.6634	13.3647	13.0756	12.8018
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	12.9262	12.6046	12.3001	12.0091
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	14.2378	13.9506	13.6749	13.4107

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; ^b'A' represents activation energy in kJ mol⁻¹. ^cStandard uncertainties are $u(A) = 0.22$ kJ/mol, $u(T) = 0.02$ K, and $u(m_a) = 0.03$ mol kg⁻¹, where m_a represents the molality of the organic solvent.

in 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD is negligible even at higher doses (500 kGy).

A similar experiment was repeated with 4.72 mol kg⁻¹ of nitric acid to mimic the real scenario, where the nitric acid concentration of HLLW is ~ 4.72 mol kg⁻¹. The nitric acid (4.72 mol kg⁻¹ initial)-extracted organic phases were subjected to gamma irradiation, followed by the determination of the viscosities of the irradiated organic phase. The results are shown in Table 16. The viscosity of 0.15 mol kg⁻¹ of TODGA/*n*-DD shows a marginal increase up to 250 kGy dose followed by more increase at 500 kGy, which can be attributed to the formation of polar degradation products that enhances the polar–polar attractive interactions in the organic phase. In short, the viscosity increases with absorbed dose at a given temperature. However, the viscosity variation is less noticeable in 0.29 mol kg⁻¹ of DOHyA/*n*-DD compared to 0.15 mol kg⁻¹ of TODGA/*n*-DD system. On the other hand, the viscosity of 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD barely increases with the radiation dose.

3.2.4. Viscosity of Nd(III)-Extracted Organic Phase at Various Absorbed Dose Levels. The organic phases (individual as well as combined solvent system) were pre-equilibrated with 1.05 mol kg⁻¹ of nitric acid, followed by Nd(III) extraction with 1.05 mol kg⁻¹ of nitric acid containing 0.019 mol kg⁻¹ of Nd(III). The Nd(III)-extracted organic phases were exposed to various absorbed gamma doses. The irradiated organic phases were further subjected to viscosity measurements at various temperatures, and the results are illustrated in Table 17. It can be seen that the irradiated organic phases have higher viscosities than the corresponding

unirradiated solvent systems. The results also revealed that all organic phases become more viscous upon irradiation. The concentration of Nd(III) in the aqueous phase was increased from 0.006 to 0.032 mol kg⁻¹, and the metal-extracted organic phases were subjected to gamma irradiation. The viscosity measurements were performed, and the results are tabulated in Table S6. It was observed that the viscosity increases with the concentration of Nd(III) in the extracted organic phase. On the basis of the above results, it can be inferred that the variation in the viscosity and density in the 0.15 mol kg⁻¹ of TODGA/*n*-DD solution changes to some extent upon irradiation, but the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD solvent system shows only a marginal change in these values.

3.3. Activation Energy, Enthalpy, and Entropy of Viscous Flow. The slope of the $\log \eta$ vs $1/T$ plot and the plot of activation energy as a function of different absorbed doses (0–500 kGy) can be used to calculate the activation energy needed for the viscous flow for the individual and combined solvent system (without any equilibration) and is illustrated in Table 18.^{38,39} It was observed that the activation energy decreases with the increase in absorbed gamma dose. The effects of temperature on these interactions appear to be small for the irradiated solvents as compared to the unirradiated case. Therefore, the activation energy of the organic phase dropped with increase in the absorbed gamma dose. The activation energy of viscous flow which can be correlated with the molecular interaction in the system opposing the flow of liquid decreases with the increase in the absorbed dose. At a higher dose, disintegration of the molecules occurs, leading to

the disruption in the molecular interactions, and introduces disorder, which is responsible for the drop in the activation energy of viscous flow under irradiated conditions.^{38,39}

In order to gain more insight into the changes in the activation energy of Nd(III)-extracted solvent systems, the variation of activation energy of viscous flow for 0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of DOHyA/*n*-DD, and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD with the absorbed dose is shown in Table 19. The organic phase

Table 19. Variation in the Activation Energy of Viscous Flow of Organic Phases as a Function of Absorbed Dose^{a,b}

organic phase contacted with 0.006 mol kg ⁻¹ of Nd(III) in 4.72 mol kg ⁻¹ of HNO ₃	activation energy/kJ mol ⁻¹			
	0 kGy	100 kGy	250 kGy	500 kGy
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	13.41	13.28	12.68	13.85
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	13.25	12.88	12.11	13.78
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	15.58	15.48	15.72	15.78

^aThe organic phase alone after equilibration was irradiated to various absorbed dose levels. Organic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD, 0.29 mol kg⁻¹ of DOHyA/*n*-DD, or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD; aqueous phase: 0.006 mol kg⁻¹ Nd(III) in 4.72 mol kg⁻¹ of HNO₃. 'A' represents activation energy in kJ mol⁻¹. ^bStandard uncertainties are $u(A) = 0.25$ kJ/mol, $u(T) = 0.02$ K, and $u(m_a) = 0.03$ mol kg⁻¹, where m_a represents the molality of the organic solvent.

was irradiated to various dose levels after being equilibrated with 4.72 mol kg⁻¹ of nitric acid containing 0.006 mol kg⁻¹ of Nd(III) solution. The results revealed that the activation energy of viscous flow for 0.15 mol kg⁻¹ of TODGA/*n*-DD and 0.29 mol kg⁻¹ of DOHyA/*n*-DD marginally decreases up to 250 kGy and then slightly increases at 500 kGy dose. However, the activation energy barely changes with the radiation dose in the case of 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD. This may be due to the fact that upon Nd(III) extraction into the organic phase, there may be an increase in the ordering of aggregates due to polar–polar interactions, which tends to increase the viscosity. On the other hand, the increase in the radiation dose may also decrease the viscosity by disintegrating the aggregates. Therefore, there is a slight decrease of viscosity up to 250 kGy in both the individual systems. At 500 kGy, the slight increase in the activation energy may be due to the formation of numerous hydrophilic degradation products which may increase the ordering of aggregates in the system. In the case of 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD, there is little variation in the activation energy with the radiation dose, which suggests that the system is more resistant

to changes in the molecular interactions upon irradiation. However, more studies are needed to understand and establish the observed behavior.

3.4. Thermodynamic Functions for Irradiated Systems. The temperature dependency on the viscosity of the liquid can be expressed as follows using the Eyring theory of reaction rate (eq 3):

$$\Delta G^* = RT \ln \left(\frac{\eta \nu}{h N_A} \right) \quad (3)$$

where R , T , ν , and η stand for the universal gas constant, the absolute temperature, the molar volume of the solution, and dynamic viscosity, respectively, and (G^*) is the Gibbs energy of activation.⁴² Equation 4 can be used to find the molar volume of a mixture.

$$\nu = \sum_{i=1}^n \frac{(x_i M_i)}{\rho} \quad (4)$$

where x_i , ρ , and M_i are the mole fraction of component i , the density of the solutions, and the molecular mass of the component i . The value of the Gibbs energy of activation (G^*) was estimated using the aforementioned formulas for the individual and 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD in the temperature range of 298 to 323 K. Table 20 depicts variation in G^* with temperature for the systems outlined above. Moreover, G^* can be related to the entropy of activation (S^*) and enthalpy of activation (H^*) by eq 5.

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (5)$$

Hence, from the plot of (ΔG^*) versus T , the intercept gives the value of (ΔH^*) and the slope gives the value of ΔS^* , which are given in Table 21.

Table 21. Enthalpy and Entropy of Activation of Viscous Flow of the Solvent Systems^{a,b}

organic phase	$\Delta H^* \times 10^{-3}$ (J mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	12.84	14.24
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	12.11	15.41
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	13.38	13.42

^aOrganic phase: 0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD. ^bStandard uncertainties are $u(\Delta H) = 0.25$ J/mol, $u(\Delta S^*) = 0.5$ J mol⁻¹ K⁻¹, $u(T) = 0.02$ K, and $u(m_a) = 0.03$ mol kg⁻¹, where m_a represents the molality of the organic solvent.

Table 20. Variation in the Gibbs Energy of Activation for Viscous Flow for All Individual Solvent Systems (0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD) as a Function of Temperature^{a,b}

organic phase	Gibbs energy of activation/J mol ⁻¹					
	298 K	303 K	308 K	313 K	318 K	323 K
0.15 mol kg ⁻¹ of TODGA/ <i>n</i> -DD	17,087.5	17,150.4	17,218.3	17,289.6	17,365.4	17,442.8
0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	16,707.8	16,778.8	16,853.0	16,931.2	17,009.8	17,093.1
0.15 mol kg ⁻¹ of TODGA + 0.29 mol kg ⁻¹ of DOHyA/ <i>n</i> -DD	17,389.9	17,446.5	17,512.1	17,576.8	17,648.5	17,725.4

^a" G_A " represents the Gibbs energy of activation in J mol⁻¹. ^bStandard uncertainties are $u(G_A) = 0.25$ J/mol, $u(T) = 0.02$ K, and $u(m_a) = 0.03$ mol kg⁻¹, where m_a represents the molality of the organic solvent.

Table 22. Variation of Excess Viscosity, Excess Molar Volume and Excess Free Energy of Activation of Viscous Flow for 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD with Temperature^a

temperature (K)	excess viscosity (Pa s) × 10 ³	excess molar volume (m ³ mol ⁻¹) × 10 ⁶	excess free energy of activation of viscous flow (J mol ⁻¹)
298	-3.75	-0.07	206.35
303	-2.79	-0.29	159.26
308	-2.14	-0.47	135.93
313	-1.65	-0.67	119.93
318	-1.28	-0.91	138.55
323	-0.99	-0.01	193.79

^aStandard uncertainties are $u(T) = 0.02$ K and $u(m_a) = 0.03$ mol kg⁻¹, where m_a represents the molality of the organic solvent.

The Gibbs free energy of activation was computed for all solvent systems (0.15 mol kg⁻¹ of TODGA/*n*-DD or 0.29 mol kg⁻¹ of DOHyA/*n*-DD or 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD), and the results are shown in Table 20. It can be seen that the Gibbs energy of activation increases linearly with the increase in temperature. The enthalpy and entropy of activation for the individual systems and combined solvent system in *n*-DD were determined and compared with each other. It was noted that the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD system showed an increase in the enthalpy of activation, which can be attributed to the enhanced intermolecular attractive forces, such as polar–polar interactions among the molecules. Furthermore, the entropy of activation, which can be correlated with the degree of disorder, is higher for individual solvent systems when compared to the combined solvent system. This may be due to the increase in polar–polar attractive interactions in the case of 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD, which decreases the disorderness of molecules.

3.5. Excess Thermodynamic Parameters. Extensive work has been carried out by several researchers on the excess thermodynamic parameters which provide insight into the molecular forces acting in the solvent systems.³⁹ Excess volume in a liquid mixture signifies interactions among the components present in the liquid mixture.³⁹ The strong polar interactions such as hydrogen bonding and complex formation between the components present in the liquid mixture leads to a reduction in the excess volume. Conversely, the weaker dispersive forces contributes to a significant excess volume due to their less disruptive nature. These types of molecular interactions collectively govern the overall excess volume observed in liquid mixtures.^{39,42} Similar to this, structural modifications of the components in a solution due to fitting of component molecules into each other's structure result in volume reduction and lead to a negative excess volume. Equation 6 can be used to define the excess volume.

$$V^E = V_{\text{mix}} - \sum_{i=1}^n x_i V_i \quad (6)$$

where V_{mix} is the molar volume of the mixture and x_i and V_i are the mole fraction and molar volume of component i , respectively. The variation in the excess volume for 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD is depicted in Table 22. It was found that there is a steady increase in the negative excess volume of 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD up to 318 K followed by a sudden decrease at 323 K. This may be due to the strong interactions caused by H-bonding which are dominant in 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD. Moreover, a

temperature rise of up to 318 K may induce the components in the solution mixture to rearrange compactly, resulting in a larger negative excess volume. Further increase in temperature may cause an enhanced randomness in the system, which would increase the magnitude of excess volume at 323 K. The negative excess volume in 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD can be attributed to the attractive interactions among the molecules than predicted by ideal mixing. In addition, a change in temperature can influence the molecular motion and thermal energy, thereby affecting the magnitude of the negative excess volume. An increase in temperature may enhance these attractive forces in a mixture with negative excess volume (indicative of attractive interactions), causing molecules to come even closer together. This may lead to a overall reduction in the volume of the mixture compared to what would be predicted by ideal mixing at that temperature. Conversely, a decrease in temperature might reduce the attractive forces, allowing molecules to move apart from each other, and may result in a slightly higher volume than predicted by ideal mixing. In a nutshell, temperature can influence the negative excess volume in 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD due to the presence of the attractive interactions between the molecules in the liquid mixture. Excess viscosity is defined by eq 7.

$$\eta^E = \eta_{\text{mix}} - \sum_{i=1}^n x_i \eta_i \quad (7)$$

where η_{mix} is the viscosity of the mixture and x_i and η_i represent the mole fraction and viscosity of component i in the mixture, respectively.

Table 22 shows the variation in excess viscosity in the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD system. The results reveal that the combined solvent system shows a decreasing trend of negative excess viscosity with temperature. The negative excess viscosity often results from the loss of polar–polar interactions in the combined solvent system, may be due to the difference in the shape and size of the components. Furthermore, the hydrogen bonding interactions originally present in the DOHyA system may get disrupted by the addition of TODGA molecules in the combined solvent system. However, with the increase in the temperature, the molecules undergo random motion and rearrangement, due to which the value of excess viscosity approaches 0. The excess free energy of activation for viscous flow for the combined solvent system shows positive values with the increase in temperature, which can be attributed to the less specific interactions, such as hydrogen bonding, which may disrupt at higher temperatures. Interestingly, a sudden increase in the excess free energy of activation at 323 K was

observed, which implies a change in the organization of the solvent structure.

4. CONCLUSIONS

0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD composed of TODGA and DOHyA in *n*-DD was considered as an efficient solvent phase for the separation of trivalent actinides and lanthanides from HLLW. To elucidate the physico-chemical properties of the system, the viscosity and density of the solvent was determined as a function of temperature at various levels of absorbed gamma doses. The results thus obtained were compared with the results obtained for the corresponding individual TODGA and DOHyA solvent systems in *n*-DD. The viscosity and density values decreased with the increase of temperature. The density and viscosity of TODGA decreased from 905 to 882 kg m⁻³ and 0.132 to 0.0363 Pa s, whereas that of DOHyA decreased from 903 to 885 kg m⁻³ and from 0.023 to 0.0084 Pa s, respectively, with the temperature increment from 298 to 323 K. The addition of *n*-DD enhanced the suitability of these solvent systems for plant applications by optimizing the density and viscosity. 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD showed higher density and viscosity values compared to individual systems owing to polar–polar interactions. The nitric acid-saturated 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD showed an increase in both density and viscosity with an increase in the initial nitric acid concentration. In the vicinity of the third-phase formation limit, both the viscosity and density increase, which can be attributed to the increase in the average aggregate size, thereby offering resistance to flow due to interaggregate polar–polar interactions. Similar results were obtained in the case of Nd(III) extraction, where the viscosity and density increased due to the increase in polar–polar interactions. During the gamma radiolysis studies, all above systems showed an increase in both density and viscosity values upon increasing the gamma dose and a gradual decrease in their values with the increase in temperature. The increase in the irradiation dose induced the production of polar molecules by degradation of the extractants, which perhaps led to the increase in density and viscosity owing to extensive polar–polar interactions operating in the solution. The increase in these thermophysical properties was only marginal, thus demonstrating the considerable stability of this solvent system towards radiation. Interestingly, the increase in density and viscosity was found to be only marginal in the case of the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD system. Additionally, the molecular interactions operating within the individual as well as combined solvent system were probed by evaluating different thermodynamic parameters like activation energy of viscous flow, excess volume, and excess viscosity. The higher activation energy of viscous flow for the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD system compared to the individual system showed that the former system is less vulnerable to change in viscosity with increase in temperature, whereas the excess parameters suggested weak molecular interactions prevailing in the same. In accordance with the findings of the present study, it can be inferred that the 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD system composed of TODGA and DOHyA in *n*-DD form a unique extractant system that is quite stable to changes in thermophysical properties such as density and viscosity upon irradiation. Thus, a detailed analysis of the thermophysical

properties provides an understanding of the suitability of the extractant systems for the purpose of nuclear reprocessing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.3c00359>.

Additional experimental results on the density and viscosity measurements carried out in TODGA/*n*-DD, DOHyA/*n*-DD, 0.15 mol kg⁻¹ of TODGA + 0.29 mol kg⁻¹ of DOHyA/*n*-DD at various experimental conditions (PDF)

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Author Contributions

P.N. played a key role in the methodology, investigation, formal analysis, and writing aspects of the study. S.M. contributed significantly to the analysis, data curation, and validation processes. K.R.S. was involved in carrying out the measurement of density and viscosity of the samples, conceptualization, investigation, data curation, validation, and draft editing. T.P. also contributed to the methodology, investigation, data curation, and validation phases. D.N. and R.L.G. were responsible for validation and draft editing. R.L.G. also provided the facility for carrying out the measurement of density and viscosity. Finally, K.A.V. played a pivotal role in

conceptualization and supervision and was actively involved in writing and reviewing the manuscript.

Notes

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