



Technical Note

Exothermic processes in nitric acid solutions imitating highly active raffinate

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ABSTRACT

The thermal stability of nitric acid solutions after contact with non-irradiated and irradiated tributyl phosphate (TBP) and its solution in Isopar-M has been studied. It has been established that exothermic processes occur during heating due to the interaction of soluble radiolysis products and the decomposition of the extractant with nitric acid. Such processes can occur at temperatures below 100 °C, but unlike a thermal explosion that occurs in seconds, they are longer in time and are accompanied by weak heat evolution. Their intensity depends on the composition of the extractant, the concentration of HNO₃, and the volume ratio of the organic and aqueous phases. The presence of extractant degradation products in raffinates does not pose a risk of a rapid evolution of gaseous products during evaporation, however, the presence of reducing agents can significantly increase the intensity of the exothermic decomposition of raffinates.

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1. Introduction

Modern technology for the reprocessing of spent nuclear fuel from nuclear power plants (NPP SNF) is based on the Purex process, in which 20–40% tributyl phosphate (TBP) solution in an inert diluent is used as an extractant [1–5]. The extraction system is subjected to high radiation and chemical loads, leading to the formation and accumulation of impurities in it, which worsen its hydrodynamic characteristics and selectivity. In this regard, the extraction mixture is constantly regenerated within the extraction cycle by washing with soda, however, part of the degradation products is not removed during such treatment and gradually accumulates in it [6,7]. The main role in the deterioration of the hydrodynamic characteristics of the extractant is played by the products of radiation-chemical decomposition of hydrocarbon diluents, among which the main contribution is made by the products of oxidation, nitration, and mixed products of interaction with TBP [1,8–12], which also worsen the characteristics of fire and explosion safety (FES). In Refs. [7,11,13,14], the main products of radiation and radiation-thermal decomposition of the extraction mixture of 30% TBP in the Isopar-M diluent and their influence on the parameters of the FES have been determined.

Dibutylphosphoric (HDBP) and monobutylphosphoric (H₂MBP) acids, carboxylic acids, ketones, carbonyl compounds, and hydrocarbons have been found among the products [7]. Specific products of radiolysis are TBP dimer and alkyl adducts of dibutyl phosphate, and specific products of thermolysis are ethylbenzene and xylenes [13]. The products of nitration, nitroxilation, hydroxylation, dealkylation, carbonylation, carboxylation, and radical dimerization during 3-year exposure of an irradiated TBP solution in Isopar-M saturated with 3.4 M nitric acid have been identified [14].

At radiochemical plants (RCP), an aqueous phase with organics dissolved in it can be formed as a result of contact of the extractant with nitric acid solutions of metals. According to Ref. [12], when the equilibrium organic phase (TBP) was heated, 60–70% TBP, HDBP, carboxylic acids (propionic - CH₃CH₂COOH, acetic - CH₃COOH), butyl nitrate and trace amounts of H₂MBP were found among the condensed products of the interaction of a mixture of extracted HNO₃ with TBP.

Even more water-soluble degradation products of extractants are formed during their irradiation [1,9,10,15]. For two-phase systems “TBP in the diluent – HNO₃”, this leads to additional effects of gas evolution due to the thermochemical decomposition of the radiolysis products of TBP and the diluent, which are distributed between the organic (OP) and aqueous phases (AP). They are characterized by the absence of an induction period, a decrease in the temperature of the onset of gas evolution, and a time-separated intense evolution of gases from the aqueous and organic phases. It

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has been established that the volumes of gaseous products released from the aqueous phase of irradiated systems are commensurate with the volumes of gaseous release from the organic phase [16], so the volumes of gaseous products released from a two-phase system irradiated to a dose of 1.3 MGy are quite large and reach $5\text{--}7 I_{\text{gas}}/I_{\text{liq}}$, and more than half of the released gases are formed during the oxidation of radiolysis products in the aqueous phase. The presence of reactive dissolved organic degradation products of the extractant in the aqueous phase can significantly increase the intensity of exothermic processes at the stage of evaporation of nitric acid solutions.

Thus, at the RCP in the process of using the extractant, its degradation occurs, and the products of the radiation-chemical decomposition of the extraction mixture pass into the aqueous phase (raffinates). The raffinates are evaporated to reduce the volume of liquid radioactive waste. It is known that APs containing reducing agents are, under certain conditions, capable of intense exothermic processes that create emergency situations [17–19]. Such accidents occurred at the RCP, and raffinates were nitric acid solutions with reducing agents, so it is important to study the thermal stability of not only the organic phase, but also the highly active raffinate. The aim of this study is to answer the questions – whether nitric acid solutions containing water-soluble degradation products of the extractant are capable of intense exothermic reactions and whether they affect the rate of decomposition of nitric acid solutions with reducing agents.

2. Experimental methods

TBP, 99% purity, grade “for laboratory use” (ACROS) and Isopar-M – isoparaffin diluent fraction C13–C14 (ExxonMobil) were used. All other used reagents were chemically pure and intended for laboratory use. Organic solutions: TBP; TBP saturated with $4 \text{ mol L}^{-1} \text{ HNO}_3$; 30% TBP in Isopar-M; 30% TBP in Isopar-M, saturated with $4 \text{ mol L}^{-1} \text{ HNO}_3$ were preliminarily irradiated on RCM-gamma-20 device (FSUE RADON) at a temperature of $25 \pm 2^\circ\text{C}$ in a cylindrical glass vessel equipped with a water seal and filled with an aqueous solution of $4 \text{ mol L}^{-1} \text{ HNO}_3$ to an absorbed dose of 1 MGy and a dose rate of $9.4 \pm 0.4 \text{ kGy/h}$.

Aqueous phases for analysis were prepared by mixing of 4, 8, and $12 \text{ mol L}^{-1} \text{ HNO}_3$ with non-irradiated or irradiated to a dose of 1 MGy organic solution in three contacts for 30 min, each time with a new portion of the organic phase. Mixing was carried out on a programmable rotator followed by gravitational phase separation.

The volume ratio of the organic phase to the aqueous phase was 1:1 (5 ml: 5 ml) to simulate real conditions and 6:1 (6 ml: 1 ml) to maximize the transition of water-soluble degradation products from the extraction mixture into the aqueous phase. After separation, the aqueous phase was taken for thermal analysis. To increase the transition of organic substances into the aqueous phase, non-irradiated solutions of TBP and 30% TBP in Isopar-M were kept for 4 h at 60°C with $12 \text{ mol L}^{-1} \text{ HNO}_3$ at a phase ratio of 1:1. In one sample, 50 g/L of acetohydroxamic acid (AHA) was added, which is used in the extraction process to change the valence of metals. To analyze the effect of uranyl nitrate (UN) on the thermal stability, a weighed portion of UN was dissolved in 1 ml of the aqueous phase, obtained after contact with an irradiated solution of 30% TBP in Isopar-M, to a concentration of 800 g/L (for salt).

Simplified aqueous solutions imitating raffinate were studied:

AP1 – aqueous phase after contact with irradiated pure TBP;

AP2 – aqueous phase after contact with irradiated pure TBP, saturated with $4 \text{ mol L}^{-1} \text{ HNO}_3$;

AP3 – aqueous phase after contact with irradiated solution of 30% TBP in Isopar-M;

AP4 – aqueous phase after contact with irradiated solution of

30% TBP in Isopar-M, saturated with $4 \text{ mol L}^{-1} \text{ HNO}_3$;

AP01 – $12 \text{ mol L}^{-1} \text{ HNO}_3$ after contact with non-irradiated pure TBP;

AP03 – $12 \text{ mol L}^{-1} \text{ HNO}_3$ after contact with non-irradiated solution of 30% TBP in Isopar-M;

AP01T – aqueous phase after heating at 60°C for 4 h of $12 \text{ mol L}^{-1} \text{ HNO}_3$ with non-irradiated pure TBP;

AP03T – aqueous phase after heating at 60°C for 4 h of $12 \text{ mol L}^{-1} \text{ HNO}_3$ with non-irradiated 30% TBP in Isopar-M;

AP3AHA – aqueous phase AP3 with dissolved 50 g/L AHA;

AP3_UN – aqueous phase AP3 with dissolved 800 g/L UN (for salt).

Degradation products were determined using a Trace 1310 gas chromatograph with a flame ionization detector and an ICQLT quadrupole mass spectrometer. Capillary columns ThermoTG-5MS (15 m length, 0.25 mm inner diameter, $0.25 \mu\text{m}$ phase thickness) and TG-SQCGC (30 m length, 0.25 mm inner diameter, $0.25 \mu\text{m}$ phase thickness, in the case of a flame ionization detector) were used. The carrier gas was helium at a constant flow (1.5 ml/min or 1.2 ml/min in the case of a flame ionization detector). The analysis was carried out in the stream splitting mode (split factor 10) and without stream splitting. The time without stream splitting was 1 min, then the split factor was set to 5. The temperature of the injector was constant and amounted to 275°C . The following gas chromatograph oven temperature program was used: 50°C for 2 min, then heating ($15^\circ\text{C}/\text{min}$) to 320°C , and exposure at 320°C for 5 min. Mass spectrometric detection was performed using electron impact ionization (70 eV EI) in the mass range of 35–650 amu. The temperature of the ion source and adapter was maintained at 200°C . Data collection was carried out in total ion current (TIC) mode. Target compounds were identified based on retention indices (RI) and mass spectra (retention time (RT) and RI in the case of a flame ionization detector). The NIST Reference Database 11.0 and the NIST Webbook were used.

The organic degradation products of the irradiated mixtures in the aqueous phase were studied on IR Prestige-21 infrared (IR) spectrometer (Shimadzu). The source was a 0.5 mW helium-neon laser with a wavelength λ_w 632.8 nm (JDU Uniphase). The spectra were recorded (single-beam recording scheme) using CaF₂ glasses and a cuvette with a lead gasket 0.129 mm thick. The error of the method does not exceed 3%.

To determine the characteristics of exothermic processes occurring in the test samples at above atmospheric pressure, a DSC-500 differential scanning calorimeter (Samara State Technical University) and a Netzsch 449 F5 Jupiter synchronous thermal analysis device were used. A $5 \mu\text{L}$ aliquot was placed in a sealed steel crucible and heated at a rate of $2^\circ\text{C}/\text{min}$ in the temperature range of $50\text{--}250^\circ\text{C}$. A similar empty crucible served as a comparison sample. To process the results, the Proteus Netzsch and TSS software packages were used, in which, using the TDpro medium, the temperature of the onset of the exothermic effect (T_{st} , $^\circ\text{C}$) and the value of the specific thermal effect (Q , J/g) were determined.

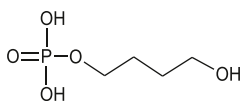
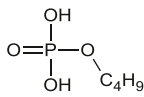
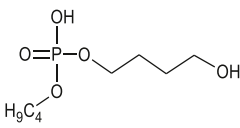
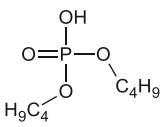
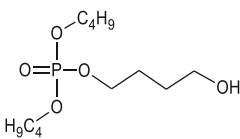
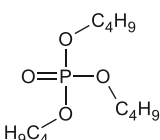
3. Results

3.1. Determination of radiolysis products in the aqueous phase

An analysis of the aqueous phase with the maximum amount of components, obtained after contact of $4 \text{ mol L}^{-1} \text{ HNO}_3$ with a solution of 30% TBP in Isopar-M irradiated to a dose of 1 MGy and saturated with $4 \text{ mol L}^{-1} \text{ HNO}_3$ (AP4) before and after evaporation by a factor of 10, was carried out by high performance liquid chromatography with mass spectrometric detection (HPLC-MS) by total ion current in the positive ionization mode. The main products and composition are given in Table 1. The following are extracted

Table 1

Composition of samples according to HPLC-MS data: AP4, evaporated by 10 times (pH = 1–2); AP4 before evaporation (pH = 1).

Compound	Release time, min	Area, %	
		AP4, evaporated by 10 times	AP4
Hydroxy-H ₂ MBP 	0.82	1.73	0.21
H ₂ MBP 	1.1	2.9	1.2
Hydroxy-HDBP 	3.3	8.5	2.1
Product 1	3.5	6.6	2.4
HDBP 	4.0	26.5	33.0
Product 2	4.9	34.5	20.7
Hydroxy-TBP 	5.8	19.1	16.8
TBP 	7.0	-0	23.7

into the aqueous phase: TBP (24% rel.), HDBP, H₂MBP, hydroxylation products of TBP, HDBP and H₂MBP, unidentified TBP derivatives, nitro compounds. The samples were also analyzed by gas chromatography-mass spectrometry (GC-MS) after the necessary sample preparation: TBP and products of its degradation were

Table 2

Characteristics of exothermic processes in the raffinate (without Isopar-M) depending on its composition: the temperature of the onset of exothermic reaction (T_{st}), the duration of the exothermic reaction (t), the heat of reaction (Q) during heating of the aqueous phases to 250 °C. The ratio of organic and aqueous phases was 6:1 for all experiments apart from AP01T which was 1:1.

Phase	[HNO ₃], mol·L ⁻¹	T_{st} , °C, ±3%	t , min, ±3%	Q , J/g, ±5%
AP01	12	–	–	–
AP01T	12	120	30	172
AP1	4	84	20	141
AP1	8	70	33	180
AP1	12	55	30	360
AP2	4	63	21	52
AP2	8	59	27	128
AP2	12	57	11	186

found, mainly products of alkylation with butyl radicals, hydroxy derivatives and isomerization products. The content of the diluent Isopar-M is low.

Organic products (carboxylic acids, ketones, esters, nitrates) were not detected by IR spectroscopy in the wavelength range from 1500 to 1800 cm⁻¹. Perhaps these products are present in negligible amounts, and the sensitivity of the device does not allow them to be detected, or they are completely absent.

Thus, almost the entire range of products identified in organic samples by HPLC-MS and GC-MS is extracted into the aqueous phase. Carbonyl compounds found in organic irradiated solutions of 30% TBP in Isopar-M are not identified in the extract from the aqueous phase.

3.2. Determination of characteristics of exothermic processes in nitric acid solutions containing water-soluble degradation products of the extractant

3.2.1. Aqueous phases after contact with TBP

The main characteristics of exothermic processes in the AP,

simulating raffinate, are presented in Table 2 depending on its composition. During heating of the AP01 obtained after contact with non-irradiated TBP, at a phase ratio of 6:1, no thermal exothermic effects were observed (Table 2). Obviously, AP01 does not contain water-soluble organic products that react with an oxidizing agent. It is known that the solubility of TBP in water does not exceed 0.4 g/L at 25 °C [20]. Exposure of the solution at 60 °C for 4 h reduces the thermal stability during subsequent thermal analysis to 250 °C in the constant heating mode (AP01T). At a temperature of 120 °C, an increase in the heat flow growth rate was recorded, which indicates the occurrence of an exothermic reaction (Fig. 1, red curve). The value of the exothermic effect was 172 J/g. This effect may indicate a significant increase in the solubility of organic components in the aqueous phase during long-term isothermal exposure.

Significantly more water-soluble products pass into the aqueous phase upon contact with irradiated TBP (AP1). With an increase in the concentration of nitric acid, T_{st} decreases and the intensity of the thermal effect of the reaction increases (Fig. 2). The maximum Q value for 12 mol L⁻¹ HNO₃ in contact with TBP irradiated to a dose of 1 MGy was 360 J/g.

Pre-saturation of irradiated TBP with 4 mol L⁻¹ nitric acid (AP2) (Table 2) generally reduces the temperature of the onset of the exothermic reaction, which is associated with the transition of a larger number of radiolysis products of the TBP-HNO₃ mixture into the aqueous phase. Linear heating of AP2 showed (Fig. 3) that an increase in the concentration of nitric acid contributes to an increase in the intensity of the heat flow without a significant change in the temperature of the onset of exothermic reactions. It is important to note that in all cases exothermic processes are prolonged in time, their rate is low, as well as gas evolution, and they begin at temperatures below 100 °C.

3.2.2. Aqueous phases after contact with 30% TBP in Isopar-M

At radiochemical enterprises, 30% TBP in an inert diluent is used for spent nuclear fuel reprocessing; for our studies, an extraction mixture of 30% TBP in the Isopar-M diluent was used. Aqueous phases for analysis were obtained by contacting of 4, 8 and 12 mol L⁻¹ HNO₃ with non-irradiated and irradiated to 1 MGy mixture of 30% TBP in Isopar-M. The results of the experiments are presented in Table 3. Since the diluent conversion products are slightly soluble in water, the main “supplier” of water-soluble products to the aqueous phase is TBP. The content of TBP in the extraction mixture is 30% by volume; therefore, a smaller amount

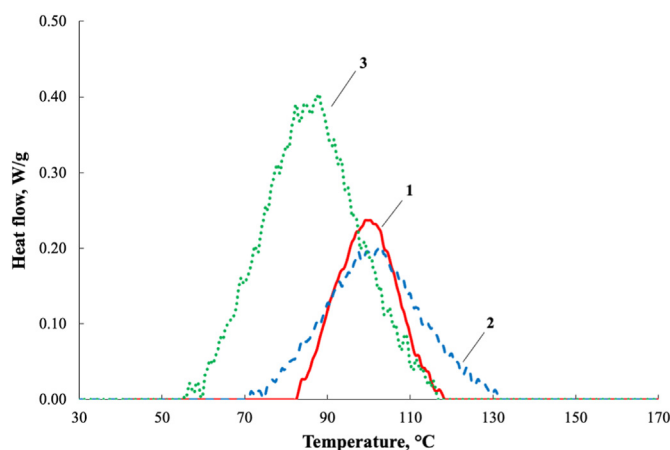


Fig. 2. Change in heat flow during heating of AP1 depending on the concentration of HNO₃ (mol·L⁻¹): 1–4; 2–8; 3–12. OP to AP ratio is 6:1.

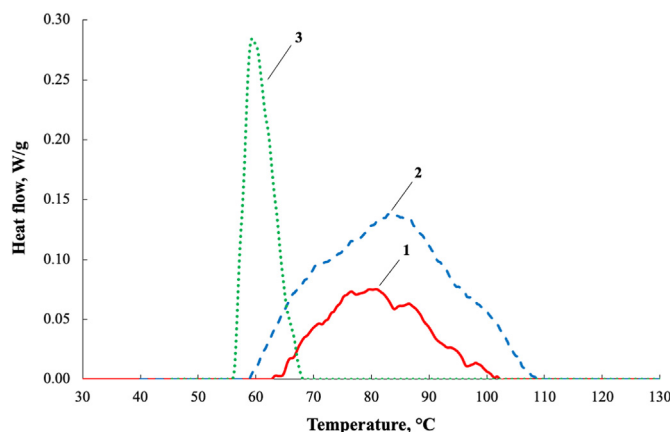


Fig. 3. Change in heat flow during heating of AP2 depending on the concentration of HNO₃ (mol·L⁻¹): 1–4; 2–8; 3–12. OP to AP ratio is 6:1.

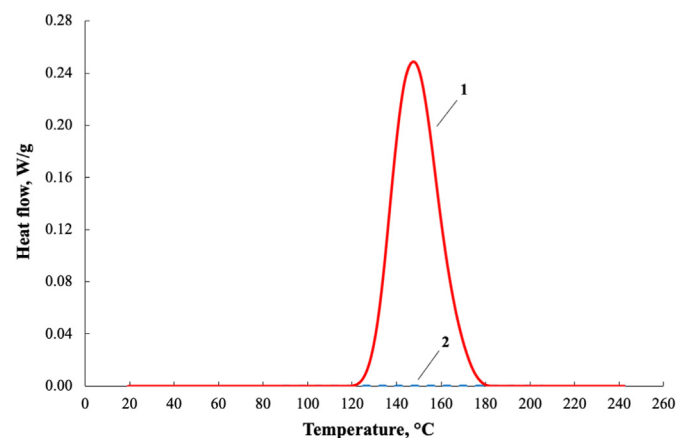


Fig. 1. Change in heat flow during heating of the aqueous phase obtained after contact of 12 mol L⁻¹ HNO₃ with non-irradiated pure TBP: 1 – with preliminary exposure at 60 °C (AP01T); 2 – without exposure (AP01).

of products is extracted into the aqueous phase. For the same reason, the value of heat evolution is 2–3 times lower than for pure TBP. The maximum Q value for AP3 and AP4 does not exceed 45 J/g.

For AP03, no exothermic effects were observed after contact with non-irradiated 30% TBP in Isopar-M. At 220 °C, an insignificant endothermic effect was recorded due to the decomposition of nitric acid. In AP03T with preliminary isothermal exposure at 60 °C, an exothermic reaction occurs, which proceeds with heat evolution.

Table 3

Characteristics of exothermic processes in the raffinate (with Isopar-M) depending on its composition: the temperature of the onset of exothermic reaction (T_{st}), the duration of the exothermic reaction (t), the heat of reaction (Q) during heating of the aqueous phases to 250 °C. The ratio of organic and aqueous phases was 6:1 for all experiments apart from AP03T which was 1:1.

Phase	[HNO ₃], mol·L ⁻¹	T_{st} , °C, ±3%	t, min, ±3%	Q, J/g, ±3%
AP03	12	—	—	—
AP03T	12	120	25	49
AP3AHA	12	125	32.5	520
AP3_UN	4	85/210	16/10	8/15
AP3	4	92	17	33
AP3	8	75	20	35
AP3	12	51	17.5	45
AP4	4	95	20	13
AP4	8	75	9	15
AP4	12	70	6	24

T_{st} of this reaction is 120 °C, the specific value of heat evolution is 49 J/g (Fig. 4).

With an increase in the concentration of nitric acid, the temperature of the onset of the exothermic reaction, as well as the maximum of the heat flow, shifts to lower temperatures (Fig. 5), which indicates the transition of radiolysis products with a lower temperature of interaction with the oxidizer to the aqueous phase. Pre-saturation of the irradiated organic phase with 4 mol L⁻¹ HNO₃ (AP4) has little effect on the parameters of the exothermic process, in contrast to solutions without diluent (AP2).

Compared to the heat evolution of the exothermic reaction between the reducing agent AHA and HNO₃, the heat evolution due to the oxidation of the degradation products of the extractant is much less (Fig. 4). Hydrolyzing to acetic acid and hydroxylamine, AHA begins to thermally decompose with heat evolution at a temperature of 125 °C. The thermal effect of the reaction is 520 J/g, which is associated with the presence of hydroxylamine in the analyzed mixture [21,22]. Its interaction with HNO₃ makes a significant contribution to the total thermal effect of the reaction (Fig. S1).

Addition of 800 g/L of UN (for salt) into AP3 has little effect on the temperature of the onset of exothermic reaction, but reduces the value of heat evolution due to an increase in the specific weight of the aqueous phase.

4. Discussion

Experiments have shown that in the extractant, when it is exposed to various production factors (interaction with oxidizing agents, heating, irradiation), products are formed, some of which are dissolved in nitric acid solutions. Such solutions, as well as other nitric acid solutions with reducing agents, under certain conditions are capable of exothermic processes, representing a potential hazard. The main part of water-soluble products is the degradation products of TBP. The qualitative and quantitative composition depends on the composition of the mixture and the type of effect on the extractant.

The interaction of non-irradiated TBP and its solutions in Isopar-M at room temperature with 12 mol L⁻¹ HNO₃ does not lead to the formation of water-soluble products. Heating of the organic phase with 12 mol L⁻¹ HNO₃ at 60 °C for 4 h leads to the appearance of products in the aqueous phase that react exothermically at 120 °C (Figs. 1 and 4).

Even more water-soluble products are formed during irradiation of the organic phase. Judging by the T_{st} values, highly reactive products are formed, the amount of which increases with an

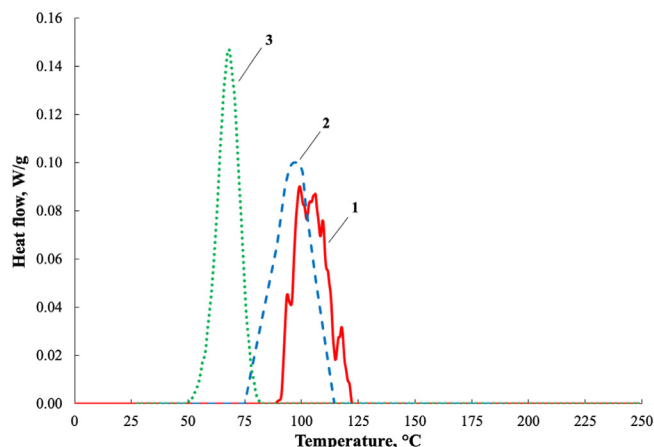


Fig. 5. Change in heat flow during heating of AP3 depending on the concentration of HNO₃ (mol · L⁻¹): 1–4; 2–8; 3–12. OP to AP ratio is 6:1.

increase in the HNO₃ concentration. The contact of the aqueous phase with the irradiated extractant, saturated 4 mol L⁻¹ HNO₃, leads to a decrease in T_{st} . According to Fig. 6, it is possible to evaluate the contribution of the components of the aqueous phase in comparison with a solution of 12 mol L⁻¹ HNO₃.

It can be seen from the experiments that the presence of the isoparaffin diluent Isopar-M increases the temperature of the onset of the exothermic process for 4 and 8 mol L⁻¹ HNO₃. At a nitric acid concentration of 12 mol L⁻¹, the temperature of the onset of exothermic reaction was close to that of the sample without diluent and amounted to 51 °C, while the value of the thermal effect was minimal and amounted to 45 J/g.

Comparison of the AP of four compositions with 4 mol L⁻¹ HNO₃ reveals a number of differences in the nature of the thermolysis (Fig. 7). Thus, the greatest thermal effect was observed for the aqueous phase of the simplest composition obtained after contact of nitric acid with irradiated TBP (AP1). It amounted to 141 J/g, which is several times higher than the thermal effects for more complex compositions. This exothermic effect is due to the transition of soluble products of TBP radiolysis into the AP: HDBP, H₂MBP, and also carried away organics. When TBP is saturated with 4 mol L⁻¹ nitric acid (AP2), the thermal effect decreases by almost a factor of three, while T_{st} shifts to lower temperatures. In this case, irradiation in the presence of nitric acid forms readily soluble

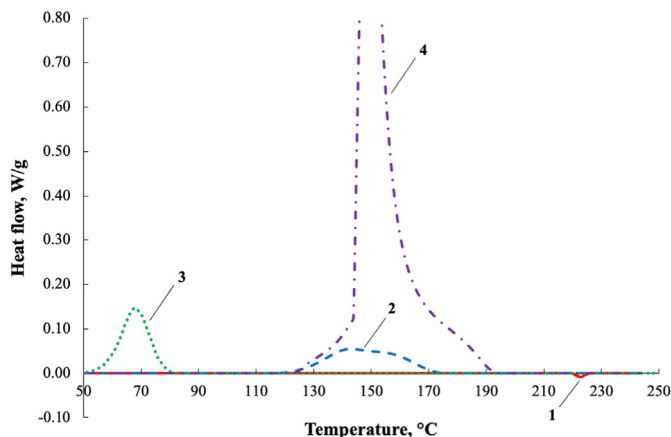


Fig. 4. Change in heat flow during heating of aqueous phases based on 12 mol L⁻¹ HNO₃: 1 – AP03; 2 – AP03T; 3 – AP3; 4 – AP3AHA.

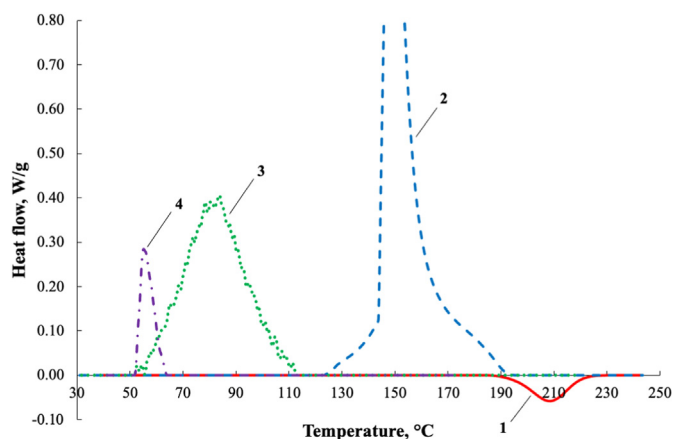


Fig. 6. Comparison of heat flow dependences during heating of aqueous solutions: 1–12 mol L⁻¹ HNO₃; 2 – AP3AHA; 3 – AP1; 4 – AP3. OP to AP ratio is 6:1.

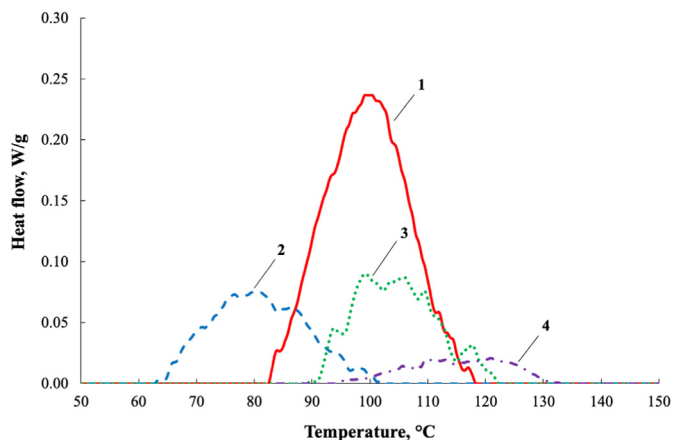


Fig. 7. Comparison of the dependences of heat flow on temperature for aqueous phases of various compositions with $4 \text{ mol L}^{-1} \text{ HNO}_3$: 1 – AP1; 2 – AP2; 3 – AP3; 4 – AP4.

radiolysis products in the form of nitro compounds [7,13,14,23], which are reactive at lower temperatures. For the compositions of AP3 and AP4, a similar picture is observed – with a decrease in the proportion of organics and the addition of $4 \text{ mol L}^{-1} \text{ HNO}_3$ to the system, the thermal effect of the reaction decreases while the value of T_{st} does not decrease. Probably, during the process of irradiation of the extractant, after contact with an extractant containing extracted nitric acid, volatile compounds are formed and a smaller amount of products that affect the exothermic character passes into the aqueous phase.

The volume ratio of the contacting phases also affects the amount of dissolved degradation products of the extractant. The thermal effects for aqueous phases obtained after contact with organics at a phase ratio of 1:1 are small. T_{st} for aqueous solutions with 4 and $8 \text{ mol L}^{-1} \text{ HNO}_3$ are close and are about 100°C , which is much higher than for solutions with $12 \text{ mol L}^{-1} \text{ HNO}_3$ (Fig. 8). The value of the thermal effect depends on the concentration of nitric acid in the aqueous phase and the composition of the initial organic phase.

Thus, in terms of absolute value, the exothermic effects during the oxidation of the degradation products of the extractant dissolved in the aqueous phase, except for AP1, are small. The duration of reactions is 10–30 min, and the rates of heat and gas evolution are insignificant. Such processes, in contrast to nitric acid solutions

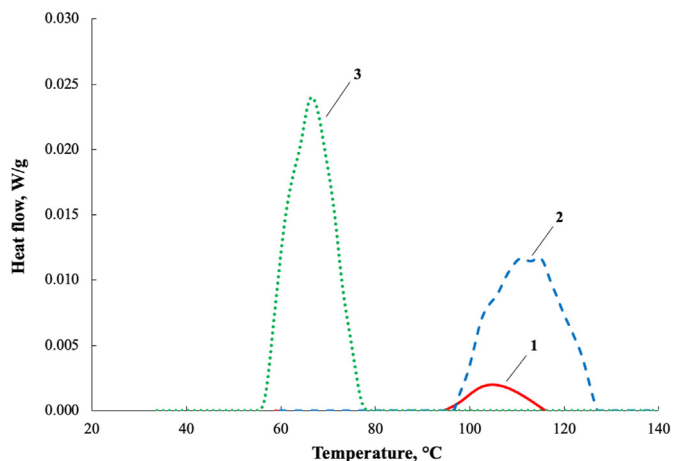


Fig. 8. Change in heat flow during heating of AP4 depending on the concentration of HNO_3 ($\text{mol}\cdot\text{L}^{-1}$): 1–4; 2–8; 3–12. The ratio of organic and aqueous phases is 1:1.

with reducing agents, are not capable of proceeding in the thermal explosion mode. In two of the mixtures tested: AP1 with $12 \text{ mol L}^{-1} \text{ HNO}_3$, and when 50 g/L AHA was present in AP3 (AP3AHA), the Q value is higher than $300 \text{ J/g}_{\text{mixture}}$, which classifies them as potentially dangerous substances in relation to the possible development of a thermal explosion [24,25].

5. Conclusions

The thermal stability of aqueous phases of a simplified composition imitating raffinate, which are formed during the extraction reprocessing of SNF, has been studied. The presence of exothermic effects indicates the transition of water-soluble products of radiolysis and hydrolysis of the extraction system into the AP. Analysis of the AP, after contact with an organic solution irradiated to 1 MGy , showed the presence of: TBP (24% rel.), HDBP, H_2MBP , their derivatives, an unidentified product, nitro compounds. The content of Isopar-M is small. Organic products (carboxylic acids, ketones, esters, nitrates) were not detected by IR spectroscopy.

The value of the thermal effect depends on the composition of the extraction mixture, the concentration of HNO_3 , and the volume ratio of the organic and aqueous phases. It is shown that the reactions proceed in the low-temperature region, some effects begin up to 100°C , which corresponds to the evaporation temperature of real high-level waste raffinates. In most cases, thermal effects are small, do not exceed 200 J/g , and are insufficient to heat the solution.

However, for the composition of the AP1 mixture with $12 \text{ mol L}^{-1} \text{ HNO}_3$, the amount of heat reaches 360 J/g , which is several times higher than the corresponding values for other compositions, and under certain conditions can lead to a thermal explosion [24].

With an increase in the concentration of nitric acid, the thermal effect increases and T_{st} decreases. The composition of the OP which is in contact with the nitric acid solution has a great influence. The larger the proportion of organics, the more hydrolysis and radiolysis products pass into the AP, and the higher the thermal effects, especially for AP1. The presence of the Isopar-M diluent increases the thermal stability of the raffinates. Exposure to 60°C for 4 h leads to the transition of a larger amount of organic products into the AP, which reduces its thermal stability. The addition of the AHA reducing agent to AP3 leads to a significant deterioration in the thermal stability of this mixture.

Thus, under the conditions of raffinate evaporation operations, exothermic processes of oxidation of water-soluble degradation products of the extractant do not pose a danger due to low process rates and their low intensity. However, the products of radiation degradation of TBP and the presence of macroquantities of AHA can serve as a “trigger” for an exothermic reaction that can lead to a thermal explosion.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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