



# Chemical uranium enrichment by light isotopes in a $(C_3H_6)_n$ -TBP- $HNO_3$ heterogeneous system

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## Abstract

The process of chemical uranium enrichment by light isotopes has been studied. The kinetic parameters of the adsorption of  $UO_2(NO_3)_2 \cdot 2TBP$  molecules in a heterogeneous system at the vertical interface between a polar  $HNO_3$  solution and a solid vertical surface of nonpolar polypropylene  $(C_3H_6)_n$  during the extraction of uranyl nitrate  $UO_2(NO_3)_2$  with tributylphosphate from an  $HNO_3$  solution were measured.

**Keywords** Isotope · Gamma radiation · Extraction · Isotopes abundance

## Introduction

The process of chemical enrichment of uranium with light isotopes is investigated. The most effective methods are based on the isotope exchange reaction between two valence forms of uranium that are in different phases, for example, water and organic. It has been established that if more than two uranium isotopes are present in the solution, the isotopes with the highest atomic weight are predominantly in a lower valence state, while the rest is in a higher one [1].

In 1957, R.V. Woodard carried out the isotope exchange reaction in HCl solution. The solution contained U(IV) in the form of  $UCl_4$  and U(VI) in the form of  $UO_2Cl_2$  [2]. After the ion-exchange reaction, U(IV) precipitated as  $U(C_2O_4)_2$ . The precipitate was filtered off, converted into soluble  $UCl_4$ , and used in the first stage of the process. The concentration of  $^{235}U$  during enrichment varied from 0.705 to 0.709 wt.%.

Maomi [3] in 1978 and Kawasaki [4] in 1983 developed ion-exchange chromatographic systems in which a layer of uranium was formed with reduction and oxidation zones at the upper and lower boundaries of the layer. As the layer moved along the column,  $^{238}U$  accumulated at the reduction boundary, and  $^{235}U$  was accumulated at the oxidation

boundary. With the initial content of  $^{235}U$  in a solution of 0.73 wt.%, Maomi S. has obtained a concentration of  $^{235}U$  at the oxidation boundary of 0.68 wt.%, and at the reduction boundary of 0.77 wt.% [3]. Kawasaki T.M. with the initial concentration of  $^{235}U$  in a solution of 0.72 wt.%, at the boundaries of oxidation and reduction, has obtained the  $^{235}U$  concentrations of 0.66 and 0.76 wt.%, respectively [4].

In 1989 Zhdanov A.N. has formed in the extraction chromatographic system (65% solution of TBP in RED-2 on Teflon powder – 2 M  $HNO_3 + N_2H_4$ ) a layer of two valence forms of uranium in a column with exhaustive extraction and re-extraction at the layer boundaries. At the concentration of uranium-232 in the initial solution of  $0.14 \cdot 10^{-6}$  wt.% at the outlet of the column of the rear front of U(IV), the concentration of  $^{232}U$  varied from  $0.14 \cdot 10^{-6}$  to  $0.19 \cdot 10^{-6}$  wt.% [5].

Delval in 1981 has used an extraction system of 50% TBP solution in dodecane–2 M HCl. The water phase has contained U(III) in the form of  $UCl_3$ . The organic phase contained U(IV) in the form of  $UCl_4$ . In the water phase, U(III) was oxidized by HCl to U(IV), then U(IV) was extracted with the organic phase. The organic phase was separated and U(IV) was reduced to U(III). The organic phase was then brought into contact with the spent water phase. Uranium(III) has passed from the organic phase into the water phase. With the initial  $^{235}U$  concentration in the water phase of 0.72 wt.%, Delval has obtained the  $^{235}U$  concentration of 0.69 wt.% in the water phase and 0.82 wt.% in the organic phase [6].

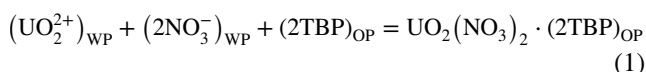
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We investigated the adsorption process of  $\text{UO}_2(\text{NO}_3)_2 \cdot (2\text{TBP})$  complexes on the nonpolar polypropylene surface of during the extraction of uranium with tributyl phosphate from a 5.6 M  $\text{HNO}_3$  solution to assess the possibility of uranium enrichment with light isotopes. Eleven heterogeneous extraction-adsorption systems with different uranium concentrations in the aqueous phase and with different concentrations of TBP in the organic phase were investigated. In total, more than a hundred samples were examined.

## Theory

If the amount of organic phase in the extraction system consisting of pure TBP and a solution of 5 M  $\text{HNO}_3$  is no more than 0.1 g per 1 L of acid solution, then all TBP is dissolved in the water phase. The TBP molecule is polar and surface active molecule. Such diphilic molecules, interacting both with polar and nonpolar media, spontaneously accumulate at an interface between polar and nonpolar phases. In our case, this is the boundary between the  $\text{HNO}_3$  solution and the wall of the polypropylene beaker  $(\text{C}_3\text{H}_6)_n$ . At this solid–liquid interface, an adsorbing layer of an ordered structure is formed [8] by TBP molecules. In the adsorption layers, TBP molecules are oriented with their polar groups towards the polar medium— $\text{HNO}_3$ , and the hydrophobic part towards the non-polar phase— $(\text{C}_3\text{H}_6)_n$ . The  $\text{UO}_2^{2+}$  ion is attached to the polar part of the TBP molecule from the  $\text{HNO}_3$  solution. The process is similar to extraction in a thin layer of TBP on the surface of polypropylene and is described by the equation:



The subscripts WP and OP mean the water and organic phases in the Eq. (1). The rate of adsorption in a heterogeneous system at the solid–liquid interface depends on the rate of molecular or convective diffusion of the reactants to the surface, and on the rate of the chemical reaction at the interface, proceeding by means of physical or chemical adsorption. If the limiting stage of adsorption is diffusion, then the process is described by a pseudo-first order equation. If the limiting stage of adsorption is a chemical reaction, then the process proceeds according to the kinetic mechanism and is described by the kinetic equation of the reaction itself. If the rates of diffusion and chemical reaction are comparable, then a mixed mechanism takes place. The suitability of implementation of kinetic models is determined by the method of data linearization in the coordinates of their equations and statistical analysis of the coefficients of determination  $R^2$ . The studies were carried out according to the pseudo-first

order model (the Erofeev-Kolmogorov equation) and according to the pseudo-second order model (the Ho and McKay equation).

## Erofeev–Kolmogorov equation

The adsorption kinetics obeys a first order equation. The greater the saturation of the surface, i.e., the smaller the difference  $(a_e - a_t)$ , the lower is the adsorption rate

$$\frac{da}{dt} = k_1(a_e - a_t) \quad \text{or} \quad \frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

In the Eq. 2,  $a_e$  and  $a_t$  are the adsorption values at the moment of established equilibrium and at the moment of time  $t$ ,  $\text{mol} \cdot \text{cm}^{-2}$ ;  $q_e$  and  $q_t$  are the amount of adsorbed substance in the organic layer at the solid–liquid interface at the moment of equilibrium establishment and at time  $t$ ,  $\text{mol}$ ;  $k_1$  is the pseudo-first order adsorption rate constant,  $\text{sec}^{-1}$ . The degree of adsorption of the  $\text{UO}_2(\text{NO}_3)_2 \cdot (2\text{TBP})$  complex at the solid–liquid interface at the solution surface was calculated by the formula:

$$\alpha = \frac{a_0 - a_t}{a_0} = \frac{C_0^{\text{WP}} - C_t^{\text{WP}}}{C_0^{\text{WP}}} = \frac{q_0^{\text{WP}} - q_t^{\text{WP}}}{q_0^{\text{WP}}} = \frac{q_t^{\text{OP}}}{q_0^{\text{WP}}} = \frac{C_t^{\text{OP}} \cdot V^{\text{OP}}}{C_0^{\text{WP}} \cdot V^{\text{WP}}} \quad (3)$$

The kinetics of  $^{234,235,238}\text{U}$  adsorption in the  $(\text{C}_3\text{H}_6)_n\text{-TBP-HNO}_3$  heterogeneous system was studied using the Erofeev–Kolmogorov equation:

$$\alpha = 1 - e^{-k_1 t^n} \quad (4)$$

or

$$C_t^{\text{WP}} = C_0^{\text{WP}} \frac{V^{\text{WP}}}{V^{\text{OP}}} (1 - e^{-k_1 t^n}) \quad (5)$$

In the Eqs. 3, 4 and 5, the quantities  $q_0^{\text{WP}}$  and  $q_t^{\text{WP}}$  are the amounts of the adsorbed substance in the aqueous phase at the initial time and at time  $t$ ,  $\text{mol}$ ;  $q_t^{\text{OP}}$  is the amount of the adsorbed substance in the organic phase at time  $t$ ,  $\text{mol}$ ;  $n$  is a constant that determines the nature of the adsorption process. For  $n > 1.1$  it is a kinetic process, for  $n < 0.9$  it is a diffusion process, for  $0.9 \leq n \leq 1.1$  it is a mixed process (the rate of a chemical reaction is comparable to the rate of diffusion) [9, 10]. In the Erofeev-Kolmogorov equation,  $k_1$  is the effective rate constant of the process, related to the reaction rate constant  $K$  by the Sakovich formula [11]:

$$K = n \cdot k_1^{1/n} \quad (6)$$

The values of  $K$ ,  $k_1$  and  $n$  were determined graphically from Erofeev-Kolmogorov equation in the linear form:

$$\ln(-\ln(1 - \alpha)) = \ln\left(-\ln\left(1 - \frac{q_t^{OP}}{q_0^{WP}}\right)\right) = \ln\left(-\ln\left(\frac{q_t^{WP}}{q_0^{WP}}\right)\right) = \ln(k_1) + n \cdot \ln(t) \quad (7)$$

The tangent of the slope of the linear graph constructed from the experimental data in the coordinates  $\ln(-\ln(1 - \alpha))$  versus  $\ln(t)$  is equal to  $n$ . The segment cut off by the graph of the function from the y-axis is equal to  $\ln(k_1)$ .

### Pseudo-second order model by Ho and McKay

The pseudo-second order equation of Ho and McKay [12] was used to describe the kinetic regularities of adsorption and reveal intermolecular interactions of the adsorbed substances [13, 14] on the overall rate of the process [15–17]:

$$\frac{t}{a_t} = \frac{1}{k_2 a_e^2} + \frac{t}{a_e} \quad (8)$$

In the Eq. (8),  $k_2$  is the pseudo-second order adsorption rate constant,  $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$ ;  $k_2 a_e^2$  is the initial adsorption rate ( $\text{mol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ ) [18]. The values of  $a_e$  and  $k_2$  were determined graphically from the experimental data plotted in the coordinates  $t/a_t$  versus  $t$ . The values of  $a_e$  and  $k_2$  were determined graphically by a linear dependence constructed from experimental data in coordinates  $t/a_t$  versus  $t$ . The slope of the straight line is  $1/a_e$ , the segment cut off by this straight line from the ordinate axis is  $1/(a_e \cdot k_2)$ . Ho and McKay's model suggests that the rate of uranium adsorption is limited by a chemical reaction occurring due to ion exchange or electron exchange between the adsorbent and adsorbate [17].

### Estimation of the accumulation rate of uranium isotopes at the solid–liquid interface

The accumulation rate of uranium isotopes  $V$  during the adsorption of  $\text{UO}_2(\text{NO}_3)_2 \cdot (2\text{-TBP})$  molecules at

the solid–liquid interface near the surface of the liquid ( $0 < h < 10$  mm) at time  $t$  is equal to the value of the time derivative of the function  $C_t^{OP}(t)$  at this moment. To determine the value of  $V$  at any time, the experimental data were approximated by the modified Langevin function

$$y = y_0 + L \cdot \left(\coth z - \frac{1}{z}\right) \quad (9)$$

In the Eq. (9):  $z = \frac{t-x_c}{s}$ ;  $t$  is the phase contact time. The rate of the adsorption process  $V$  at time  $t$  was calculated by the formula:

$$V(t) = \frac{dy(t)}{dt} \quad (10)$$

## Experimental

### Materials and reagents

For the experiment, an initial solution of uranyl nitrate  $\text{UO}_2(\text{NO}_3)_2$  in 5.58 M  $\text{HNO}_3$  (TS) was prepared. It has contained uranium in the amount of 107.31 mg/mL. The isotopic composition of uranium in the initial solution was  $^{234}\text{U}$ ,  $0.0016 \pm 0.0003$  at.%;  $^{235}\text{U}$ ,  $0.471 \pm 0.007$  at.%;  $^{238}\text{U}$ ,  $99.5 \pm 0.3$  at.%. Water phases of samples of heterogeneous extraction-adsorption working systems  $\text{HNO}_3\text{-TBP-(C}_3\text{H}_6)_n$  were prepared from the initial solution. The composition of the water and organic phases of the working systems is shown in Table 1. The following designations are used in the Table 1:  $V_{\text{TS}}$  is the volume of the initial solution of  $\text{UO}_2(\text{NO}_3)_2$  in 5.58 M  $\text{HNO}_3$  taken to prepare the water phase, mL;  $V_{\text{HNO}_3}$  is the volume of nitric acid with density of 1.40 g/mL or 14.92 mol/L, mL;  $V_{\text{H}_2\text{O}}$  is the volume of distilled water, mL;  $C_{\text{U}}$  is the concentration of uranium in the water phase in units of mg/mL and mol/L;  $V_{\text{TBP}}$  and  $V_{\text{GG}}$  volume of TBP and “galosha” gasoline used to prepare the organic phase, mL.

**Table 1** Composition of working solutions of uranium

Sample of system	Aqueous phase						Organic phase	
	$V_{\text{TS}}$ , mL	$V_{\text{HNO}_3}$ , mL	$V_{\text{H}_2\text{O}}$ , mL	$C_{\text{U}}$ , mg/mL	$C_{\text{U}}$ , mol/L	$C_{\text{HNO}_3}$ , mol/L	$V_{\text{TBP}}$ , mL	$V_{\text{GG}}$ , mL
PP1	4	9	11	17.885	0.0751	6.60	1	0
PP1a	4	9	11	17.885	0.0751	6.60	0.7	0.3
PP1b	4	9	11	17.885	0.0751	6.60	0.9	0.1
PP2	8	9	7	35.770	0.150	7.53	1	0
PP4	2	9	13	8.943	0.0376	6.14	0.7	0.3
PP6	3	9	12	13.414	0.0564	6.37	0.7	0.3
PP7	5	9	10	22.356	0.0939	6.83	0.7	0.3

For the experiment, 24 mL of water phase and 1 mL of organic phase (pure TBP or a solution of TBP in “galosha” gasoline) were poured into a 50 mL polypropylene beaker. The pouring of the organic phase into the beaker starts the phase contact time. The process was carried out under static conditions without shaking.

## Instruments

The gamma-ray spectra of the samples analyzed were measured with the coaxial p-type HPGe-detector of 20% relative efficiency (GC2018, Canberra, USA) and energy resolution of 1.7 keV at the 1332.5 keV line of  $^{60}\text{Co}$  coupled with multichannel digital analyzer (Lynx, Canberra, USA). The spectra were processed using the Genie-2000 software.

The secondary X-ray spectra of the samples were measured with HPGe detector (PGT, Princeton Gamma-Tech Instruments, Inc., USA) of 30 mm<sup>2</sup> active area and energy resolution of 200 eV at the 6.4 keV K $\alpha$  X-ray line of Fe. Secondary X-ray radiation of the samples was excited by an external X-ray source based on radionuclide  $^{109}\text{Cd}$  (XCd9.233). The radioactivity of the  $^{109}\text{Cd}$  in the source was 0.36 GBq.

## Measurement of the uranium concentration distribution profiles at the solid–liquid interface and in the volume of the aqueous phase along the beaker symmetry axis

Aliquots of the studied solutions and aliquots of standard solutions of uranyl nitrate in water were applied to sheets of polyethylene terephthalate film GOST 24234-80. The volume of aliquots was 50  $\mu\text{L}$ . The films with the samples' aliquot and the films with the standard solutions' aliquots were subsequently placed on the X-ray spectrometer sample

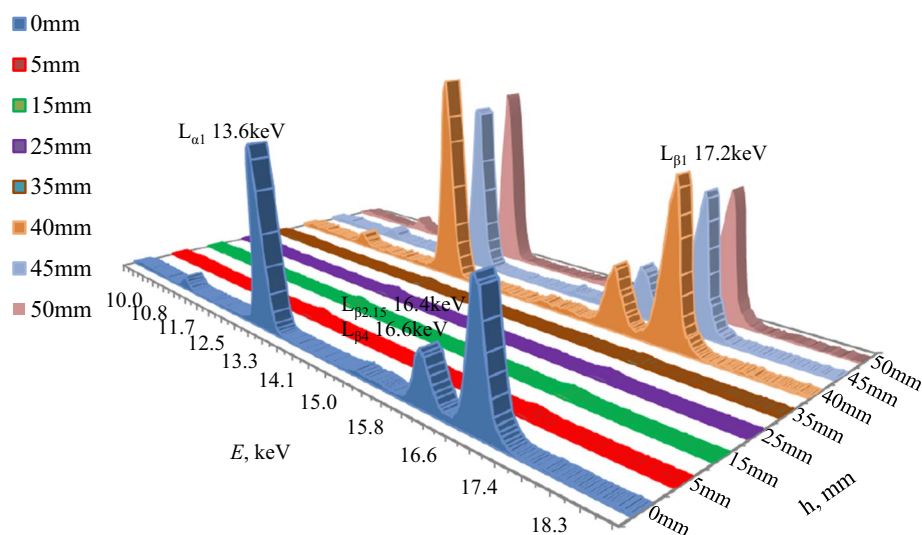
holder. The spectra of secondary X-ray emission of the samples and standards were consistently registered. The secondary X-ray lines of uranium in the spectrum of aliquots taken at the solid–liquid interface at a depth  $h$  from the solution surface are shown in the Fig. 1. The spectra were normalized to registration time one second.

The uranium concentration in the sample was calculated by the formula  $C = \frac{I_{\text{sam}} \cdot CF_{\text{sam}}}{K}$  where  $I_{\text{sam}}$  is the counting intensity in the analytical line of secondary X-ray radiation of uranium in the spectrum of the sample under study;  $K = \frac{I_{\text{st}} - \Delta I}{C_{\text{st}}}$  is the tangent of the slope angle of the calibration graph in coordinates  $I_{\text{st}}$  vs.  $C_{\text{st}}$ ;  $\Delta I$  is a intercept cut off by the calibration graph on the ordinate axis;  $CF = \frac{-\ln \alpha}{1 - \alpha}$  is the attenuation coefficient of X-ray radiation in the substance;  $\alpha = \exp\left[-\left(\frac{\mu_{\gamma}}{\cos \phi} + \mu_X\right)L\right]$  is the transmission coefficient of exciting and analytical X-rays;  $\mu_{\gamma}$ ,  $\mu_X$  – linear attenuation coefficients of external exciting radiation and analytical X-ray radiation of uranium, cm<sup>-1</sup>;  $L$  is the thickness of the sample;  $\phi$  is the angle of incidence of the exciting X-ray radiation on the sample.

## The measurement of the isotopic composition of uranium at the solid–liquid interface and in the aqueous phase along the symmetry axis of the polypropylene beaker

To determine the isotopic composition of uranium, 10–50  $\mu\text{L}$  aliquots of the solution were applied to the strips of filtering paper, packed into polyethylene bags, and placed on the detector of a gamma-ray spectrometer with low-background passive shielding [19]. The spectrum registration time was 2–5 days. The isotopic composition of uranium was determined from the analytical lines of gamma radiation of radionuclides from the equilibrium decay chains of  $^{234}\text{U}$ ,  $^{235}\text{U}$  and

**Fig. 1** The secondary X-ray lines of uranium in the spectrum of aliquots taken at the solid–liquid interface at a depth  $h$  from the surface of the solution



**Table 2** Analytical  $\gamma$ -radiation of radionuclides from equilibrium decay chains of  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  [20]

The chain	The analytical nuclide	$E_\gamma$ , keV	$\gamma_{\text{abu}}$ , %
$^{234}\text{U}$	$^{234}\text{U}$	53.231	0.119
$^{235}\text{U}$	$^{235}\text{U}$	143.786	10.53
	$^{235}\text{U}$	109.178	1.5
	$^{235}\text{U}$	163.379	4.855
	$^{235}\text{U}$	185.739	53.15
	$^{235}\text{U}$	205.333	4.7
$^{238}\text{U}$	$^{234}\text{Th}$	63.288	3.812
	$^{234}\text{Th}$	83.307	0.0702
	$^{234}\text{Th}$	92.353	2.725
		92.778	2.688
	$^{234\text{m}}\text{Pa}$	766.412	0.2067
	$^{234\text{m}}\text{Pa}$	1000.997	0.889

$^{238}\text{U}$  (Table 2). The Table 2 uses the following designations:  $E_\gamma$  is the energy of analytical gamma radiation, keV;  $\gamma_{\text{abu}}$  is the yield of gamma quanta per one decay of a radioactive nucleus, %.

In the equilibrium decay chains of uranium, the radioactivity of any daughter nuclide is proportional to the radioactivity of the original parent uranium radionuclide. The isotopic composition of uranium (at. %) is calculated by the formula:

$$C_i = \frac{N_i \cdot 100}{N_{234} + N_{235} + N_{238}} \quad (11)$$

where  $N_i$  is the number of  $^i\text{U}$  atoms in an aliquot ( $i=234, 235, 238$ ). The value of  $N_i$  was calculated from the condition  $A_i = \lambda_i \cdot N_i$ , where  $A_i$  is the activity of  $^i\text{U}$ , Bq;  $\lambda_i$  is the decay constant of  $^i\text{U}$ . The activity of uranium isotopes  $^i\text{U}$  (Bq) was calculated from the activity of radionuclides of the equilibrium decay chain according to the formula  $A_i = \frac{S_i}{t \cdot \frac{\gamma_{\text{abu}}}{100} \cdot \text{eff}} \cdot \frac{P_{di}}{100}$  where  $S_i$  is the area of the analytical peak of the radionuclide

from the equilibrium decay chain  $^i\text{U}$  in the gamma-ray spectrum of the aliquot;  $t$  is the spectrum registration time, sec;  $\gamma_{\text{abu}}$  is the yield of gamma quanta per one decay of a radioactive nucleus, %;  $\text{eff}$  is the detector efficiency, relative units;  $P_{di}$  is the decay probability of the daughter radionuclide in the chain relative to the decay of the initial nucleus  $^i\text{U}$ : for  $^{231}\text{Th}$   $P_{di} = 100\%$  in the  $^{235}\text{U} \rightarrow ^{231}\text{Th}$  chain; for  $^{234}\text{Th}$   $P_{di} = 100\%$  in the  $^{238}\text{U} \rightarrow ^{234}\text{Th}$  chain; for  $^{234\text{m}}\text{Pa}$   $P_{di} = 99.89\%$  in the  $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234\text{m}}\text{Pa}$  chain; for  $^{234}\text{Pa}$   $P_{di} = 0.16\%$  in the  $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{Pa}$  chain.

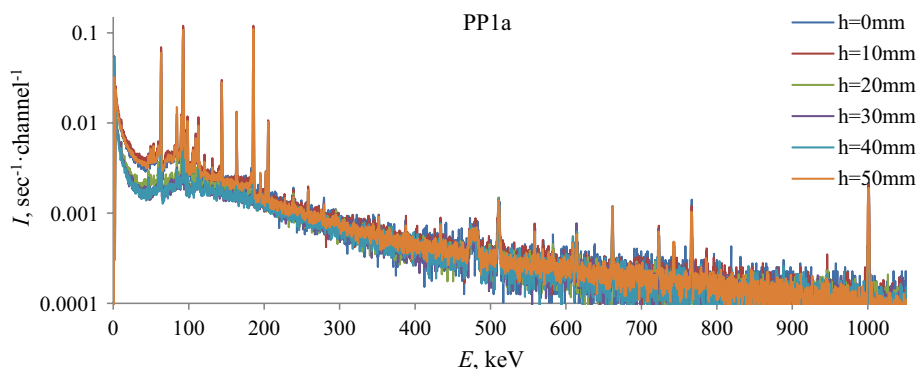
When calculating the isotopic composition of uranium, it was assumed that the activities of all radionuclides correspond to the equilibrium state of decay chains.

The Fig. 2 shows the gamma-ray spectra of aliquots of the organic phase. Aliquots were taken in the PP1a system at the solid–liquid interface, at depth  $h$  from the surface of the liquid in the plastic beaker. The aliquots volume was 50  $\mu\text{L}$ . The spectra were normalized to registration time of one second.

### The measurement of kinetic parameters of $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$ adsorption at the solid–liquid interface

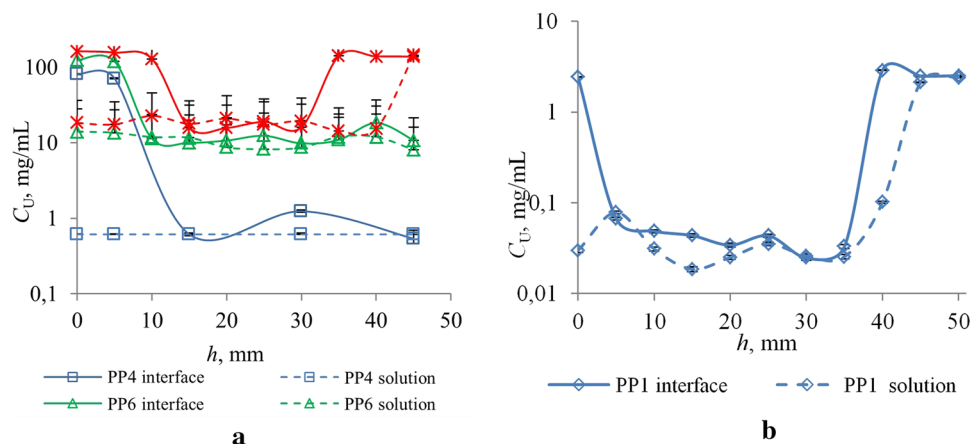
The adsorption of  $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$  was carried out under static conditions without shaking. The kinetic parameters of adsorption were determined experimentally by the dependence of the adsorption value  $a$  on the phase contact time  $t_c$ . The adsorption value  $a$  was calculated as the number of moles of uranium in the organic layer at the interface per unit area of the layer at a given time. For this, the aliquots of the organic phase were taken from the solid–liquid interface near the solution surface at specified times during the adsorption of  $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$ . The kinetic parameters of adsorption were determined by a graphical method according to the pseudo-first order model of Erofeev-Kolmogorov and also to the pseudo-second order model of Ho and McKay.

**Fig. 2** Gamma-ray spectra of the aliquots from the solid–liquid interface. PP1a system, the surface of the solution is at  $h=0$  mm





**Fig. 3** Uranium concentration distribution in the  $(C_3H_6)_n$ -TBP- $HNO_3$  system



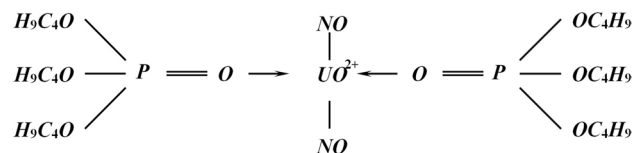
## Results and discussion

### The distribution profile of uranium concentration at the solid–liquid interface and in the aqueous phase on the symmetry axis of the polypropylene beaker

With the volume of the organic phase of 1 mL and inner diameter of the polypropylene beaker of 26 mm, the thickness of the organic phase layer should be 1.9 mm. But in the extraction system  $HNO_3$ -TBP with the ratio of water and organic phases 24 : 1, there is no sharp border between the water and organic phases. The Fig. 3a and b show the distribution profiles of the uranium concentration at the solid–liquid interface (solid lines) and in the water phase on the symmetry axis of the polypropylene beaker (dashed lines). The values at  $h=0$  mm correspond to the liquid surface. The phase contact time  $t_c$  was more than 10 days.

The Fig. 3a and b demonstrate the accumulation of uranium at the vertical solid–liquid interface near the surface of the liquid and at the bottom of the beaker in the  $(C_3H_6)_n$ -TBP-5.58 M  $HNO_3$  adsorption system. The accumulation of uranium at the solid–liquid interface, near the surface of the liquid, is due to the fact that at 25 °C the pure TBP is partially soluble in water (0.39 g/L). TBP molecules form an organic layer on the surface of polypropylene due to physical adsorption. Since the density of TBP is less than the density of the water phase, a layer is formed near the surface of the solution. Further, according to the extraction mechanism in a thin layer of the extractant,  $UO_2(NO_3)_2 \cdot (2 \cdot TBP)$  molecules accumulate on the polypropylene surface. In the  $UO_2(NO_3)_2 \cdot (2 \cdot TBP)$  molecule, the electron-donor oxygen atom of the phosphoryl group in the TBP molecule forms a donor–acceptor bond with the extracted uranium (Fig. 4) [21].

The accumulation of uranium at the bottom of the beaker (Figs. 3 and 5) is due to the fact that with an excess of uranium in the water phase and at small amount of TBP



**Fig. 4** Uranyl nitrate disolvate

**Fig. 5** An example of a system in which an organic phase has accumulated at the bottom of a polypropylene beaker



molecules in the organic phase, almost all TBP molecules are bound into  $UO_2(NO_3)_2 \cdot (2 \cdot TBP)$  complexes which, with an increase in the contact time of the phases, leads to growth of the density of the organic phase.

The data for calculation of the maximum density of the organic phase  $\rho_{TBP}$  after extraction of uranyl nitrate  $UO_2(NO_3)_2$  by tributylphosphate are given in the Table 3.

The densities of organic and water phases were determined by the pycnometric method after equilibration of the system. For the working system PP6, the density of organic phase at the bottom of the beaker was  $1.26 \pm 0.02$  g/mL, and the density of the water phase in the center of the beaker was  $1.20 \pm 0.02$  g/mL. For the PP1 system, the density of the organic phase at the bottom of the beaker was  $1.58 \pm 0.01$  g/mL, and the

**Table 3** Calculation of the maximum value of  $\rho_{\text{TBP}}^{\text{U}}$ 

Parameter	Value
The number of TBP molecules in 1 mol of the organic phase before extraction	$N_{\text{TBP}} = \frac{\rho_{\text{TBP}}}{M_{\text{TBP}}} \cdot N_a = 2.22 \cdot 10^{21}$
The number of molecules of the $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$ complex in 1 mol of the organic phase after extraction	$N_{\text{TBP}^{\text{U}}} = \frac{\rho_{\text{TBP}^{\text{U}}}}{M_{\text{TBP}^{\text{U}}}} \cdot N_a$
Restrictions according to Eq. (1)	$2 \cdot N_{\text{TBP}} = N_{\text{TBP}^{\text{U}}}$
Density of TBP	$\rho_{\text{TBP}} = 0.98 \text{ g/mL}$
Molar mass of TBP	$M_{\text{TBP}} = 266.3 \text{ g/mol}$
Molar mass of the complex $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$	$M_{\text{TBP}^{\text{U}}} = 926.7 \text{ g/mol}$
Maximum density of the organic phase after extraction	$\rho_{\text{TBP}^{\text{U}}} = 2 \cdot \rho_{\text{TBP}} \cdot \frac{M_{\text{TBP}^{\text{U}}}}{M_{\text{TBP}}} = 6.8 \text{ g/mL}$

density of the aqueous phase in the center of the beaker was  $1.16 \pm 0.02 \text{ g/mL}$ .

At uranium concentrations in the water phase of 8.94 (PP4) and 13.41 (PP6) mg/mL, the maximum concentrations of uranium at the solid–liquid interface was observed in a layer 10 mm thick near the solution surface. When the concentration of uranium in the water phase is 17.88 (PP1) and 22.36 (PP7) mg/mL, the density of organic phase at the solid–liquid interface becomes higher than the density of the water phase, after 2 or 3 days, and part of the organic phase shifts to the bottom of the beaker (Fig. 3a and b).

### Isotopic distribution of uranium at the solid–liquid interface

Due to the partial solubility of TBP in the aqueous phase, a layer of organic phase is formed at the  $(\text{C}_3\text{H}_6)_n$ –5.58 M  $\text{HNO}_3$  interface. Due to gravitational separation and different rates of adsorption of the  $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$  complex molecules at the solid–liquid interface, the formation of gradients of concentration and isotopic composition of uranium is possible ( $i = 234, 235, 238$ ). To test this assumption, three heterogeneous extraction-adsorption systems PP1, PP1a, and PP1b were prepared. The initial concentration of uranium in the water phase was 17.885 mg/mL. The phase contact time  $t_c$  was more than 10 days. The process was carried out under static conditions without shaking. The isotopic distribution of uranium at the solid–liquid interface at different depths  $h$  from the liquid surface was measured by spectrometric method, observing the intensities of analytical lines of gamma radiation  $^{234}\text{U}$  (53.2 keV),  $^{234}\text{Th}$  (92.4 and 92.8 keV),  $^{235}\text{U}$  (185.7 keV) and  $^{234\text{m}}\text{Pa}$  (1001.0 keV) in the spectra of aliquots (Fig. 6a–d). All the spectra were normalized to the registration time of one second.

For the extraction-adsorption systems PP1, PP1a, and PP1b, the changes in the concentrations of  $^{234}\text{U}$  and  $^{235}\text{U}$  at the solid–liquid interface at different distances  $h$  from the liquid surface are given in The Fig. 7a and b. The points with  $h = 0 \text{ mm}$  correspond to the liquid surface in the propylene beaker.

### Isotopic distribution of uranium in the aqueous phase on the symmetry axis of the polypropylene beaker

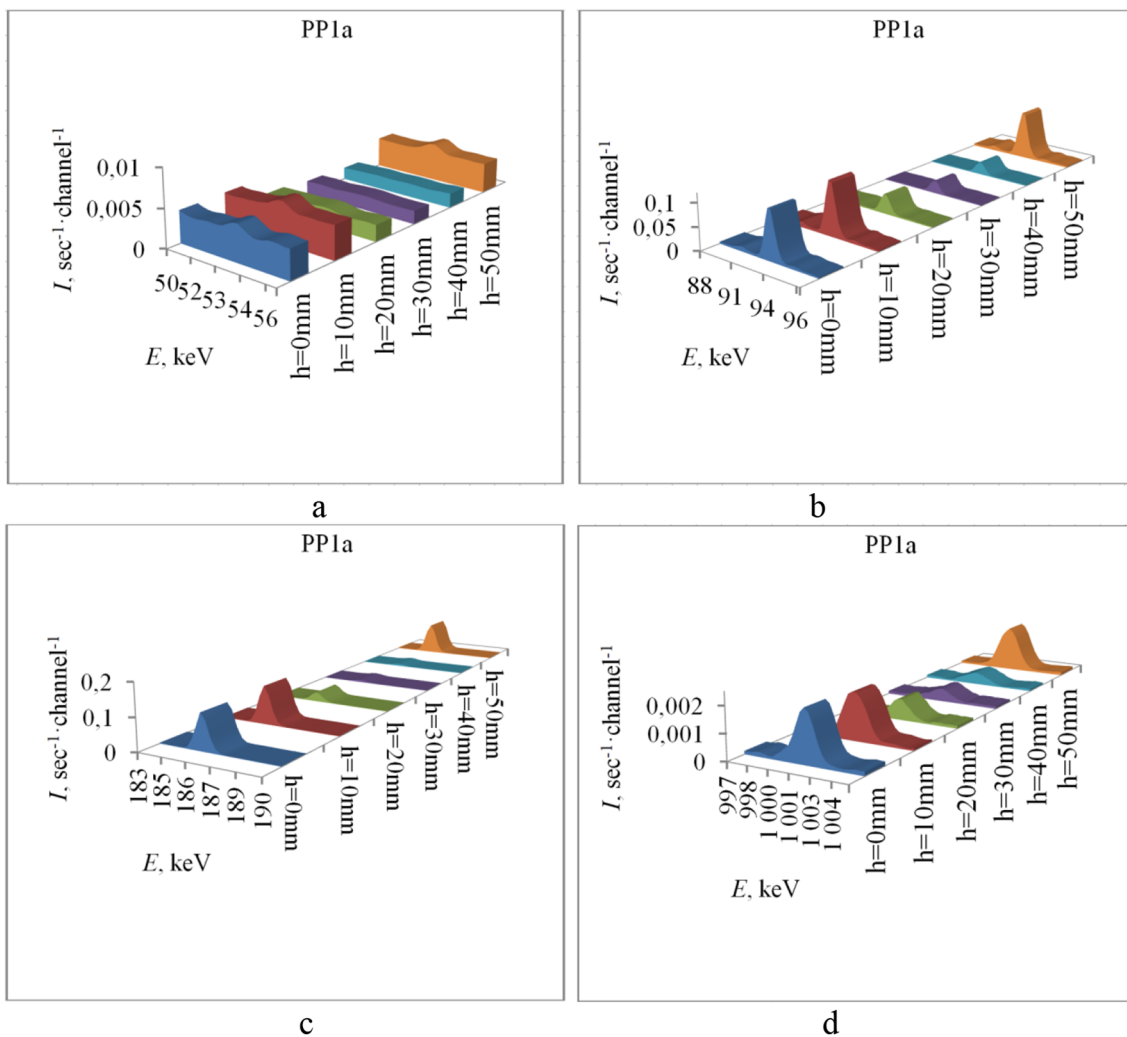
Similarly, the distribution of the isotopic composition of uranium in the aqueous phase along the symmetry axis of the polypropylene beaker was measured after equilibrium was established in the PP1a system in the direction from the liquid surface ( $h = 0 \text{ mm}$ ) to the bottom of the beaker ( $h = 50 \text{ mm}$ ). The phase contact time during the measurement was  $t_c = 9$  days. The measurement results are shown in the Fig. 8.

In the PP1 system at the bottom of the beaker  $h = 50 \text{ mm}$  (the organic phase is pure TBP), the  $^{235}\text{U}$  concentration was  $1.55 \pm 0.03 \text{ at. \%}$ , and the  $C_{235\text{U}}/C_{238\text{U}}$  ratio of  $^{235}\text{U}$  and  $^{238}\text{U}$  concentrations was  $0.016 \pm 0.002$ . There was practically no organic layer on the surface of the solution, and the entire organic phase enriched by  $^{235}\text{U}$  was accumulated at the bottom of the beaker.

In the PP1a system (the organic phase was TBP and “galosha” gasoline in the ratio of 7 : 3), the  $^{235}\text{U}$  concentration at the bottom of the beaker was  $1.58 \pm 0.01 \text{ at. \%}$ , while the  $C_{235\text{U}}/C_{238\text{U}}$  ratio was  $0.0160 \pm 0.0001$ . At the solid–liquid interface near the liquid surface, the  $^{235}\text{U}$  concentration was  $1.60 \pm 0.02 \text{ at. \%}$ , and the  $C_{235\text{U}}/C_{238\text{U}}$  ratio was  $0.0049 \pm 0.0006$ .

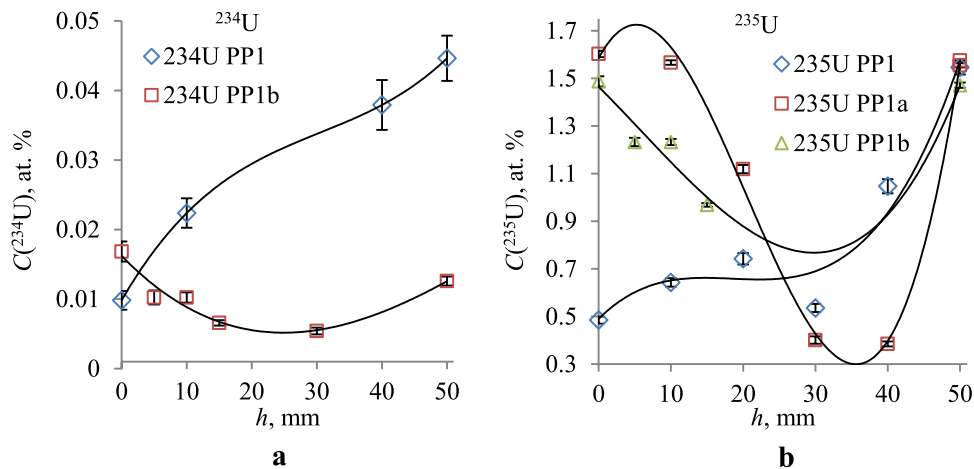
In the PP1b system (the organic phase was TBP and “galosha” gasoline in the ratio of 9 : 1), at the solid–liquid interface near the liquid surface, the  $^{235}\text{U}$  concentration was  $1.49 \pm 0.02 \text{ at. \%}$ , and the  $C_{235\text{U}}/C_{238\text{U}}$  ratio was  $0.015 \pm 0.001$ .

The distribution of  $^{235}\text{U}$  in the systems PP1, PP1a, PP1b shows that an increase of the amount of “galosha” gasoline in the organic phase leads to a decrease of the solubility of TBP in the aqueous phase, and to increase of the layer of organic phase enriched by  $^{235}\text{U}$  at the solid–liquid interface near the solution surface.



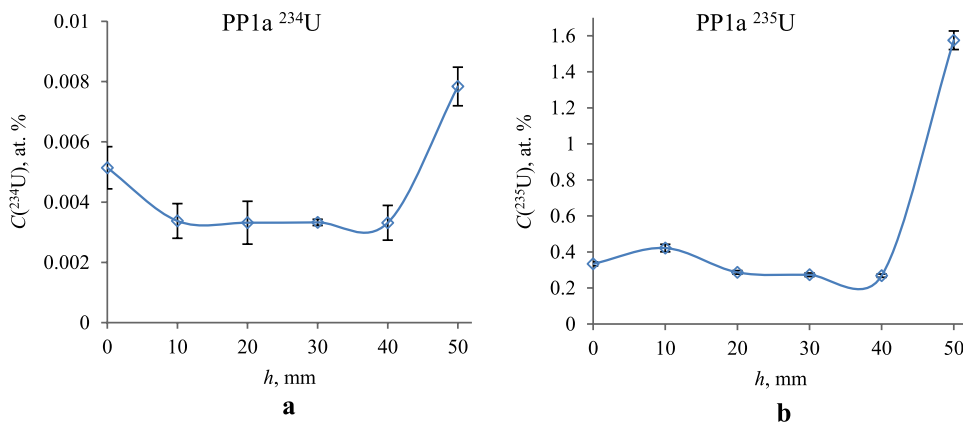
**Fig. 6** Gamma-ray lines of  $^{234}\text{U}$  (a),  $^{234}\text{Th}$  (b),  $^{235}\text{U}$  (c) and  $^{234\text{m}}\text{Pa}$  (d) in aliquot spectra sampled at the solid–liquid interface at a depth of  $h$  from the liquid surface. PP1a system

**Fig. 7** Changes in the concentrations of  $^{234}\text{U}$  (a) and  $^{235}\text{U}$  (b) at the solid–liquid interface

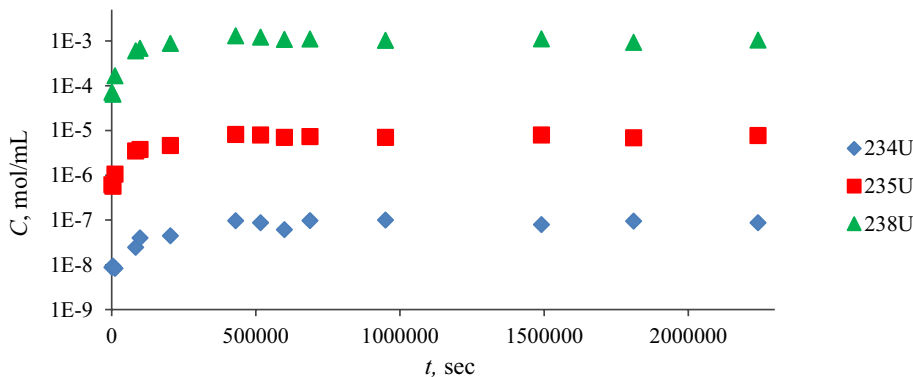




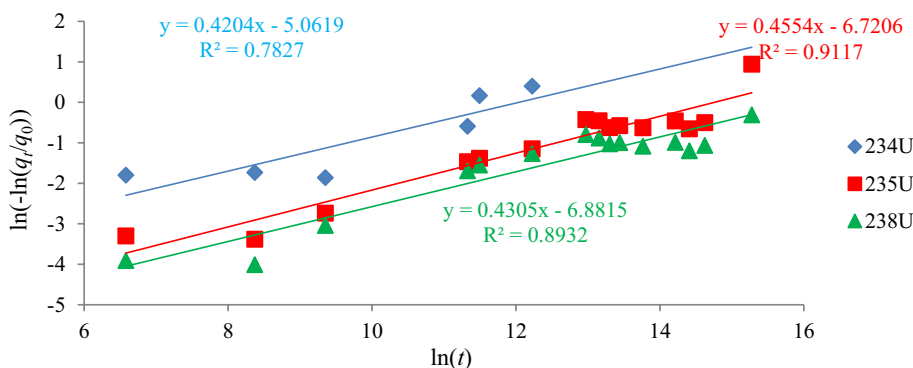
**Fig. 8** Distribution of  $^{234}\text{U}$  (a) and  $^{235}\text{U}$  (b) concentrations in the aqueous phase along the symmetry axis of the polypropylene beaker; PP1a system



**Fig. 9** Kinetic curves of adsorption at the solid–liquid interface, near the liquid surface, in PP2 system



**Fig. 10** Graphical interpretation of  $^i\text{UO}_2(\text{NO}_3)_2 \cdot (2\text{-TBP})$  adsorption at the solid–liquid interface in the coordinates of Erofeev–Kolmogorov equation; PP2 system



**Table 4** Kinetic parameters of  $^{234,235,238}\text{U}$  accumulation at the solid–liquid interface near the surface of the aqueous phase in PP2 system

Isotope	$\ln(k_1)$	$k_1$	$n$	$K$	$R^2$	Process
$^{234}\text{U}$	-5.06	$6.33 \times 10^{-3}$	0.42	$2.48 \times 10^{-6}$	0.78	Diffusion
$^{235}\text{U}$	-6.72	$1.21 \times 10^{-3}$	0.45	$1.78 \times 10^{-7}$	0.91	Diffusion
$^{238}\text{U}$	-6.88	$1.03 \times 10^{-3}$	0.43	$4.92 \times 10^{-8}$	0.89	Diffusion

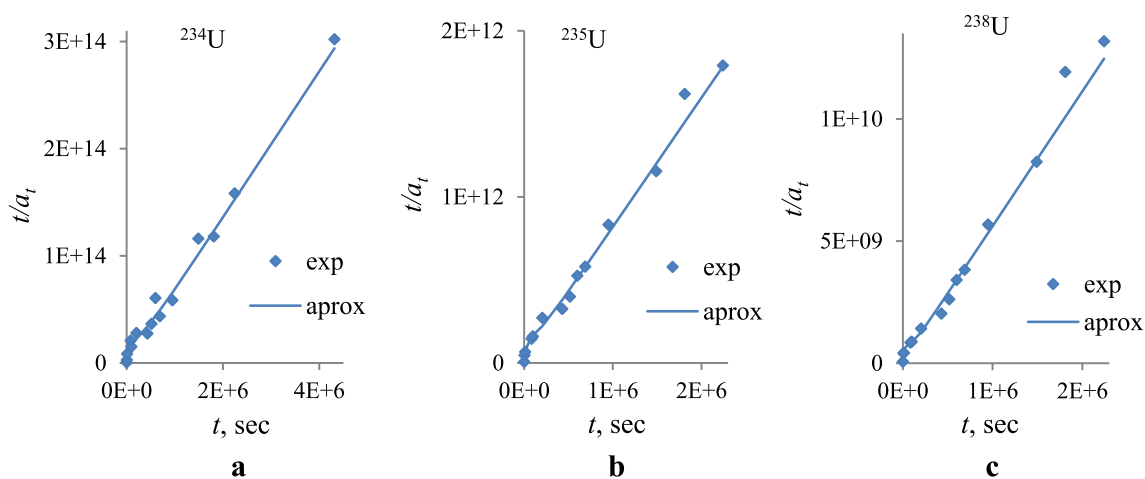
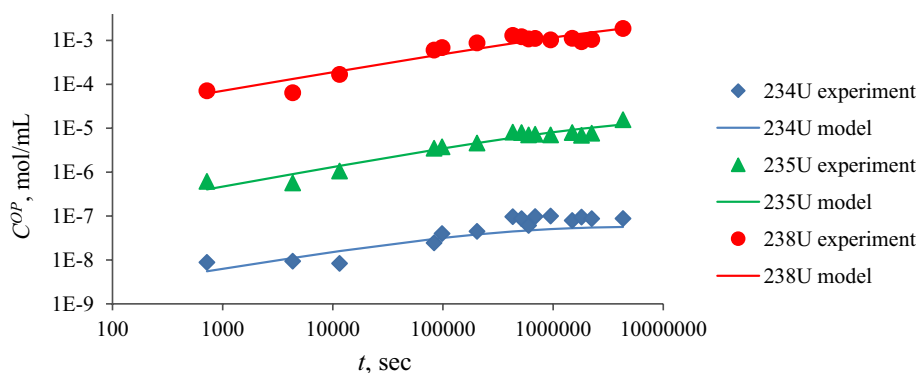
**The study of adsorption kinetics of the  $^i\text{UO}_2(\text{NO}_3)_2 \cdot (2\text{-TBP})$  complex according to the Erofeev–Kolmogorov pseudo-first order model**

The extraction rate constants  $^i\text{U}$  ( $i = 234, 235, 238$ ) from the aqueous phase during the adsorption of the  $^i\text{UO}_2(\text{NO}_3)_2 \cdot (2\text{-TBP})$  complex at the solid–liquid interface

near the liquid surface in the heterogeneous system  $7.53\text{ M HNO}_3\text{-TBP-(C}_3\text{H}_6)_n$  was determined from kinetic curves of the process (Fig. 9). To do this, the experimental data for the PP2 system were plotted in the coordinates of Erofeev–Kolmogorov equation  $\ln(-\ln(1-\alpha))$  vs  $\ln(t)$  (Fig. 10).

The results of graphical determination of the values of  $K$ ,  $k_1$  and  $n$  are given in the Table 4.

**Fig. 11** Kinetic curves of  $^{234,235,238}\text{U}$  accumulation at the solid–liquid interface in the  $7.53\text{ M HNO}_3 - \text{TBP} - (\text{C}_3\text{H}_6)_n$  system near the surface of aqueous phase in the PP2 sample



**Fig. 12** Kinetic curves of U adsorption in the coordinates of the Ho and McKay model

By series of parallel measurements, it was found that reproducibility of the measurement results for the value of  $K$  is much better than for the value of  $k_1$ . Since  $n < 0.9$ , adsorption is limited by diffusion of  $^i\text{UO}_2(\text{NO}_3)_2$  molecules in the aqueous phase to the layer of the organic phase at the liquid–solid interface near the solution surface. The values of the adsorption rate constants of 234, 235, and 238-uranium in the form of  $^i\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$  complexes on the polypropylene surface form a series in which  $K_{234\text{U}} > K_{235\text{U}} > K_{238\text{U}}$ . Experimentally measured and calculated by the Erofeev–Kolmogorov model, the kinetic curves of  $^{234,235,238}\text{U}$  adsorption at the solid–liquid interface in the PP2 heterogeneous system near the solution surface are shown in the Fig. 11.

### The pseudo-second-order model of Ho and McKay

For the PP2 system, the values of  $a_e$  and  $k_2$  were determined graphically from the experimental data plotted in the coordinates  $t/a_t$  versus  $t$  (Fig. 12).

The Table 5 lists the kinetic parameters of uranium isotopes adsorption at the solid–liquid interface near the

**Table 5** The experimental and model-calculated adsorption parameters of  $^{234,235,238}\text{U}$

Parameter	Dimension	$^{234}\text{U}$	$^{235}\text{U}$	$^{238}\text{U}$
$1/a_e$	$\text{cm}^2 \cdot \text{mol}^{-1}$	$6.79 \times 10^7$	$7.97 \times 10^5$	$5.92 \times 10^3$
$1/(k_2 \cdot a_e^2)$	$\text{cm}^2 \cdot \text{sec} \cdot \text{mol}^{-1}$	$5.65 \times 10^{12}$	$4.66 \times 10^{10}$	$6.93 \times 10^7$
$R^2$		0.99	0.99	0.99
$a_{e \text{ calc}}$	$\text{mol} \cdot \text{cm}^{-2}$	$1.47 \times 10^{-8}$	$1.25 \times 10^{-6}$	$1.69 \times 10^{-4}$
$k_2$	$\text{cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$	817	13.6	0.51
$k_2 \cdot a_e^2$	$\text{mol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$	$1.77 \times 10^{-13}$	$2.15 \times 10^{-11}$	$1.44 \times 10^{-8}$
$a_{e \text{ exp}}$	$\text{mol} \cdot \text{cm}^{-2}$	$1.47 \times 10^{-8}$	$1.26 \times 10^{-6}$	$1.80 \times 10^{-4}$

surface of aqueous phase in the PP2 system, as well as the experimental  $a_{e \text{ exp}}$  and calculated  $a_{e \text{ calc}}$  values of the equilibrium adsorption determined by the Ho and McKay model.

The data in Table 5 show that the process is well described by the pseudo-second order model, since the coefficients of determination are quite high, and the values  $a_{e \text{ calc}}$  and  $a_{e \text{ exp}}$  are in good agreement. Thus, a chemical reaction is involved in the adsorption process.

### Estimation of the accumulation rate of uranium isotopes in the organic layer at the solid–liquid interface near the surface of the aqueous phase in the PP2 system

To determine the rate  $V$  of the accumulation of uranium isotopes at any given time, the experimental data were approximated by a modified Langevin function. The approximation results are presented in the Table 6.

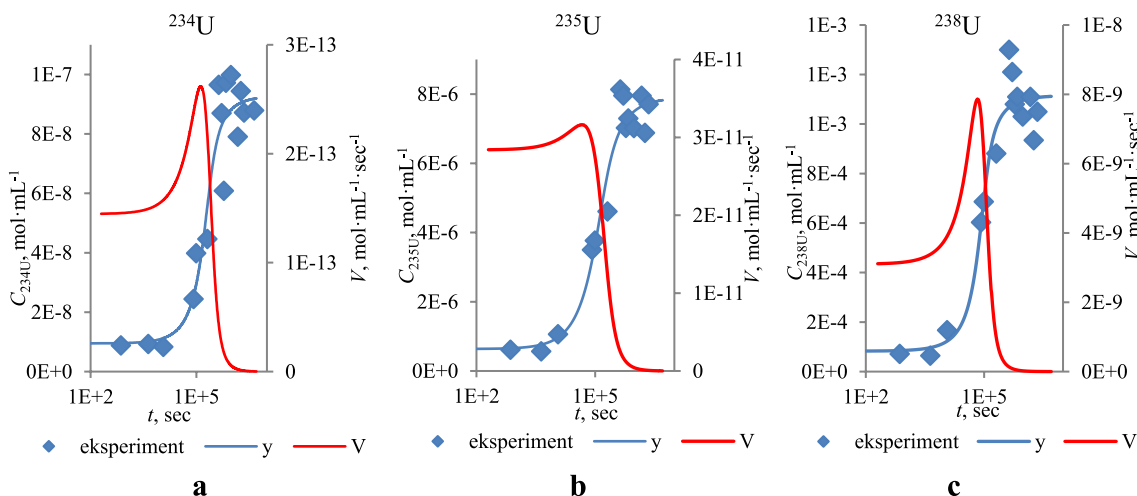
The experimental data and the values of  $y$  and  $V$  functions are shown in the Fig. 13.

In the kinetic equation  $V = k \cdot C_{TBP}^x \cdot C_U^y$ , the reaction rate constant  $k$  does not depend on initial concentration of the reagents and is equal to the reaction rate at the initial concentration of each reagent 1 mol/L [22]. The values of the function  $V(t)$  for  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$ -uranium normalized to the initial concentration  $^1\text{U}$  1 mol/L are shown in the Fig. 14.

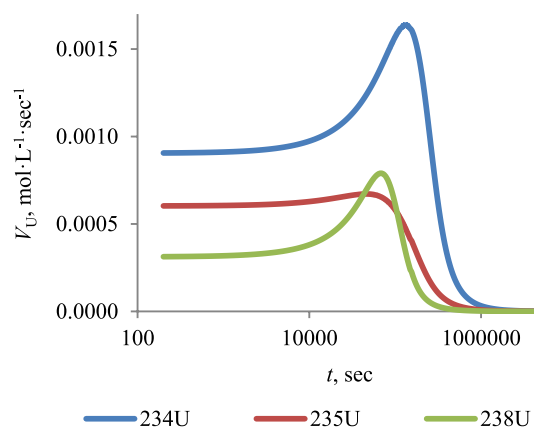
The Fig. 14 shows that the ratio between the rates of accumulation of  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$  at the solid–liquid interface near the surface of the aqueous phase can be interpreted as a series in which  $V_{234} > V_{235} > V_{238}$ . This indicates that the mobility of  $\text{UO}_2(\text{NO}_3)_2 \cdot (2 \cdot \text{TBP})$  molecules with light uranium isotopes is higher than with heavier isotopes.

**Table 6** Approximation parameters of experimental data

Isotope	$^{234}\text{U}$	$^{235}\text{U}$	$^{238}\text{U}$
$y_0$	$3.79 \times 10^{-8}$	$2.04 \times 10^{-6}$	$4.76 \times 10^{-4}$
$x_c$	132,042.78	46,024.85	68,165.53
$L$	$5.49 \times 10^{-8}$	$5.86 \times 10^{-6}$	$6.39 \times 10^{-4}$
$s$	69,833.20	61,724.51	27,103.66
$R^2$	0.91	0.96	0.95



**Fig. 13** The experimental data and the values of functions  $y(t)$  and  $V(t)$  for  $^{234,235,238}\text{U}$  adsorption in the PP2 system



**Fig. 14** The rate of accumulation of uranium isotopes in the organic layer at the solid–liquid interface near the liquid surface with initial concentration of  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  in the aqueous phase of 1 mol/L

An extraction system consisting of a solution of uranium in nitric acid and tributyl phosphate in which the number of uranium atoms is equal to twice the number of TBP molecules can be used practically to obtain a micro-quantity of uranium with an unnatural isotopic distribution. If a polypropylene film is lowered into such the extraction system, then a thin layer of organic phase with excess uranium content will form on the surface of polypropylene near the surface of the solution. When the polypropylene film is removed from the solution, a thin layer of the organic phase will partially or completely remain on its surface. This organic layer contains uranium of non-natural isotopic composition.

## Conclusions

The uranium enrichment by light isotopes during the uranium extraction of a small amount of polar organic extractant TBP from the nitric acid solution has been registered. The enrichment of uranium with light isotopes was registered during the extraction of uranium with a small amount of the polar organic extractant TBP from a solution of nitric acid. With a small amount of extractant in the extraction system, a vertical layer of the organic phase of TBP and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  molecules is formed near the surface of the solution at the polypropylene–water phase interface. In this layer, the concentration of  $^{234}\text{U}$  corresponds to  $0.045 \pm 0.003$  at. %,  $^{235}\text{U}$   $1.55 \pm 0.03$  at. %, and  $^{238}\text{U}$   $98.4 \pm 1.9$  at. %. It has been established that the adsorption rate constants of  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$  at the solid–liquid interface, calculated by the models of pseudo-first and pseudo-second order kinetics, near the surface of the aqueous phase can be presented by a series, in which  $k_{234} > k_{235} > k_{238}$ .

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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