In the processing of highly irradiated fuel in thermal and fast neutron reactors, problems arise due to the special properties of the irradiated materials [1]. The peculiarities of fuel cells in fast reactors include, in particular, a high content of fission products. Radioactive iodine makes a substantial contribution to this value. It is known that iodine is approximately 70% extracted by tributyl phosphate (TBP), is practically not reextracted with uranium and plutonium, and is not entirely washed out of the organic solutions during soda purification. Thus, iodine is accumulated in the organic phase, promoting radiolytic and, in all probability, chemical conversions of the extraction reagent. The problem of iodine in extraction technology includes the necessity of identification and study of the distribution of all forms of iodine in solutions of TBP under the action of ionizing radiation.

In this work the chemical forms of iodine formed in pure (100%) TBP in the γ-irradiation of Co\(^{60}\) were studied spectrophotometrically.

TBP and iodine were subjected to thorough purification. Deaerated solutions of iodine in TBP were irradiated on an RKhm-gamma-20 apparatus with a cobalt source. The absorbed dose rate of the radiation, measured with a ferrosulfate dosimeter, was 2.8 \(\times\) 10\(^{15}\) eV/ml·sec. Spectrophotometric measurements were conducted on an SF-4A instrument in the wavelength region \(\lambda = 210-600\) nm. To prevent the action of light, the investigated iodine solutions were stored in darkness.

The absorption spectra of solutions of iodine in TBP were measured in the absence of irradiation and under the action of the \(\gamma\)-radiation of Co\(^{60}\) on deaerated samples (Fig. 1). The optical density \(E\) was related to a thickness of the absorbing layer equal to 1 cm. The absorption spectrum of a nonirradiated solution of iodine in TBP (curve 1) is explained on the basis of the literature data as the sum of the bands reflecting the following conversions of iodine:

\[
\begin{align*}
I_2 + \text{TBP} &\rightleftharpoons \text{TBP} \cdot I_2; \quad (1) \\
\text{TBP} \cdot I_2 &\rightleftharpoons \text{TBP}^+ \cdot I^-; \quad (2) \\
\text{TBP}^+ \cdot I^- &\rightleftharpoons I_2 + \text{TBP}. \quad (3)
\end{align*}
\]

Reaction (1) was investigated spectrophotometrically in [2]. The formation of the molecular complex TBP·I\(_2\) (equilibrium constant \(K_{298} = 19.5\) liters/mole), for which an absorption band of I\(_2\) in a complex appears in the visible region of the spectrum (\(\lambda_{\text{max}} = 460\) nm), and a band of charge transfer appears in the ultraviolet region (\(\lambda < 250\) nm), was demonstrated.

It is suggested [3] that in polar media there may be an ionization of the complex [reaction (2)], followed by the formation of a triiodide, for solutions of which in ethylene chloride it has been found [4]: \(\lambda_{\text{max}} = 370\) nm (coefficient of extinction \(\varepsilon_{370} = 2.5 \cdot 10^4\) cm\(^{-1}\)·mole\(^{-1}\)·liter) and \(\lambda = 295\) nm (\(\varepsilon_{295} = 4.5 \cdot 10^4\) cm\(^{-1}\)·mole\(^{-1}\)·liter).

As it follows from Fig. 1 (curve 1), if there is no irradiation, there is little I\(_2\) in the investigated solution. When the solution is irradiated (curves 2 and 3), a more rapid process of conversion of TBP·I\(_2\) to the form I\(_2\) is observed. In the case of substantial values of the absorbed dose (curve 4), there is a breakdown of the triiodide, and further (curve 5), a transition of the dissolved iodine into a form determining absorption with \(\lambda_{\text{max}} = 260\) nm and \(\varepsilon_{260} = 400\) cm\(^{-1}\)·mole\(^{-1}\)·liter, corresponding to alkyl iodides [5].

TABLE 1. Radiation-Chemical Yield \( G_{I_3} \) of the Formation of \( I_3^- \) in TBP

<table>
<thead>
<tr>
<th>Iodine concentration in initial solution, M</th>
<th>( 1.45 \times 10^{-3} )</th>
<th>( 2.9 \times 10^{-3} )</th>
<th>( 4.0 \times 10^{-3} )</th>
<th>( 5.7 \times 10^{-3} )</th>
<th>( 8.7 \times 10^{-3} )</th>
<th>( 1.16 \times 10^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{I_3} ), 1/100 eV ...............</td>
<td>1.8</td>
<td>2.2</td>
<td>2.8</td>
<td>3.3</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The molecular coefficients of the triiodide in solutions of TBP were calculated according to the spectra of the irradiated solutions, corresponding to the total decomposition of the complex TBP \( \cdot I_3 \) and maximum accumulation of \( I_3^- \) (see Fig. 1, curve 3), which permitted a determination of the concentrations of \( I_3^- \) at various values of the absorbed dose (Fig. 2). For the linear portions of the curves of Fig. 2 (left-hand branches) the values of the radiation-chemical yield of the formation of \( I_3^- \) were calculated according to the formula

\[
G_{I_3} = \frac{\Delta C_{I_3^-} N_0 100}{\Delta D} \left( \frac{1}{100 \text{eV}} \right),
\]

where \( \Delta C_{I_3^-} \) is the change in the concentration of \( I_3^- \) (M) with change in absorbed dose \( \Delta D \) (eV/liter); \( N_0 \) is Avogadro's number. The results of the calculations are presented in Table 1.

The order of the reaction of radiation-chemical formation of the triiodide was determined according to the slope of the straight line \( \log (G_{I_3^-}) = f \log (C_I) \) and proved equal to 0.5 with respect to the iodine concentration in the initial solution. The value of the fractional order of the reaction obtained is characteristic of complex reactions proceeding through intermediate stages. Evidently the radiation-chemical process of formation of \( I_3^- \) occurs according to the scheme represented by reactions (1)-(3) and supplemented by the reaction of solvated electrons, arising during the ionization of the medium:

\[
\text{TBP} \cdot I^- + e^- \rightarrow I + \text{TBP}.
\]

A consideration of the formal kinetics of reactions (1)-(4) leads to the equation for the rate of formation of the triiodide \( v_{I_3} \sim P \cdot (I_2)^{0.5} \) (where \( P \) is the absorbed dose rate), in which the order of the reaction (0.5) corresponds to the value found experimentally.