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TRITIUM DISTRIBUTION RATIOS BETWEEN THE 30% TRIBUTYL
PHOSPHATE(TBP)-NORMAL DODECANE(nDD) ORGANIC PHASE
AND URANYL NITRATE-NITRIC ACID AQUEOUS PHASE

October 1989

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Mitsuru MAEDA and Takeshi TSUJINO

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Tritium Distribution Ratios between the 30% Tributyl
Phosphate(TBP)-Normal Dodecane(nDD)
Organic Phase and Uranyl Nitrate-Nitric Acid Aqueous Phase

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Tritium distribution ratios between the organic and aqueous phases were measured for the system of 30% tributyl phosphate(TBP)-normal dodecane(nDD)/uranyl nitrate-nitric acid water. It was confirmed that tritium is extracted by TBP into the organic phase in both chemical forms of tritiated water (HTO) and tritiated nitric acid (TNO₃). The value of tritium distribution ratio ranged from 0.002 to 0.005 for the conditions of 0-6 mol/L nitric acid, 0.5-800 mCi/L tritium in aqueous phase, and 0-125 g-U/L uranium in organic phase. Isotopic distribution coefficient of tritium between the organic and aqueous phases was observed to be about 0.95.

Keywords: Tritium, Distribution, TBP, Reprocessing, Extraction,
Tritiated Water, Uranyl, Nitric Acid

+ Office of Planning

30%リン酸トリブチル (TBP) - ノルマルドデカン
(nDD) の有機相と硝酸ウラニル-硝酸水溶液相の間
におけるトリチウム分配比

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トリチウム分配比を、30%TBP-nDD / 硝酸ウラニル-硝酸-水系で測定した。トリチウムは、トリチウム水 (HTO) とトリチウム硝酸 (TNO₃) の化学形でTBPに抽出され、その分配比は、水相中の硝酸濃度が0~6 mol/l、トリチウム濃度が0.5~800 mCi/l、有機相中のウラン濃度が0~125 g-U/lの範囲で0.002 から0.005 の間で得られた。また、このトリチウムの2相間同位体分配係数は、約0.95であった。

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1. INTRODUCTION

Tritium is one of the nuclei generated by the ternary fission in nuclear fuels(1). The tritium is released when they are dissolved in a reprocessing plant. The released tritium is diffused and diluted throughout the process. This beta-ray emitting nucleus causes many troubles in the plant maintenance and the contamination of environment. However, in the currently running reprocessing plant, the tritium is neither recovered nor retained in the plant. This isotope is able to be used as a fuel in D-T burning fusion reactors. So, it is recommended that tritium be reasonably managed and controlled in the future reprocessing plant(2).

For the purpose of retaining the tritium in the nuclear fuel reprocessing plant, two methods: the tritiated water recycle process(1-6) and the voloxidation(7,8), have been proposed. In the voloxidation method, tritium is released into the off-gas by the oxidation treatment of sheared fuels in the head-end process applied to the ordinary Purex process. Tritium introduction into the solvent extraction process can be avoided by this method. However, it is accompanied by the difficulty of handling of highly radioactive powder. As for the tritiated water recycle process, tritium is dissolved by nitric acid solution along with fuels in the dissolver. As shown in Fig. 1, the uranium bearing aqueous solution, which is contaminated with tritium, is introduced into the co-extraction step. Most tritium is separated into the high level aqueous waste (HAW), however, up to 7% (1) of the tritium flows along with the organic solvent to the uranium-plutonium partition step. In the tritiated water recycle process, the organic solvent, which flows along with uranium and plutonium from the co-extraction step, is scrubbed by a non-tritiated nitric acid solution and set back to the co-extraction step. Nitric acid is recovered from the raffinate of coextraction step by evaporation operation and recycled to the dissolution step. The recycled nitric acid is contaminated by tritium and the concentration of tritium in the recycled aqueous solution increases dependent upon the number of the recycling. Thus, tritium is retained in the reprocessing plant.

The key operation in the tritium recycle process is the tritium scrubbing step. Multi-stage extractors such as mixersettlers or pulsed-columns are applied for this operation. Tritium is able to be scrubbed by the distribution preferred to the aqueous solution rather than to the organic solvent during the contact of solutions. Equilibrium of the tritium distribution, however, has not been made clear in the literature.

As one step of establishing an effective tritium scrubbing technique, tritium distribution ratios between the organic and aqueous phases were measured in the present study. The influences of concentrations of nitric acid, uranyl nitrate, and tritium on the tritium distribution ratios are discussed.

2. EXPERIMENTAL

2.1 Experimental Procedure

Tritium distribution between the phases was investigated by the beaker-scale experiment. Figure 2 shows the procedure. Tritium in the form of tritiated water (HTO) was loaded into the experimental system. Certain amounts of uranyl nitrate, nitric acid, and tritiated water were added into the system composed of a nontritiated water and a 30 volume percent TBP diluted with nDD organic solution. A twenty milli-liter volume of each solution was mixed thoroughly by shaking for more than 2 hours so that the distribution equilibrium was attained. After the shaking stopped, the solutions were settled in a tube with plug for over 2 hours enough to separate the phases completely. Then, the concentrations of solutes in each phase were analysed. A shaker attached to a water bath was used in order to fix the solution temperature at 20 °C.

The concentration ranges of solutes in the present experiment include the standard conditions applied to the ordinary Purex process. Nitric acid concentration in the aqueous phase was varied in the range from 0 to 6 mol/L. Uranium concentration in the organic phase was from 0 to 125 g-U/L. Tritium concentration in the aqueous phase ranged from 0.5 to 800 mCi/L.

Tritium concentration was analysed by liquid scintillation counter. Nitric acid and uranium concentrations were analysed by potentiometric titration. Water content in the organic phase was analysed by Karl Fisher titration.

2.2 Experimental Results

Figure 3 shows the results for a uranium-free system. Tritium was distributed between a 30% TBP/nDD organic solvent and nitric acid solution. Nitric acid concentration in the organic phase increases in proportion to nitric acid concentration in the aqueous phase. On the other hand, water

content in the organic phase decreases by increasing the nitric acid concentration. Displacement of water by nitric acid occurs at the adsorbing agent TBP in the organic phase. Tritium distribution ratio D_T is defined by Eq. (1) in the present work.

$$D_T = \frac{\text{(Tritium concentration in organic phase)}}{\text{(Tritium concentration in aqueous phase)}} \quad (1)$$

The value of D_T increases by increasing nitric acid concentration, although tritium is loaded into the system as tritiated water. This phenomenon indicates that tritium easily exchanges between tritiated water (HTO) and tritiated nitric acid (TNO₃). Value of the obtained tritium distribution ratio agrees with that of distribution ratio of hydrogen atoms composing the water and nitric acid in both phases. Tritium atoms are, therefore, extracted into the organic phase as both chemical species of tritiated water and tritiated nitric acid.

Tritium distribution ratio D_T decreases by adding uranyl nitrate into the system as shown in Fig. 4. For this case, nitric acid concentration in the aqueous phase was constant at 1 mol/L. Uranium concentration in the organic phase increases by increasing uranium concentration in the aqueous phase. Uranyl ions displace water and nitric acid at the adsorbent TBP in organic phase. As the result, tritium distribution ratio decreases by increasing the uranium concentration.

Figure 5 shows the result for the case of 85 g-U/L uranium concentration in the organic phase, which is the standard condition of ordinary Purex process. Tritium distribution ratio D_T increases from 0.002 to 0.004 by increasing nitric acid concentration in the aqueous phase from 0 to 6 mol/L. The value of D_T obtained is about one fourth that for the uranium-free system shown in Fig. 3. Water content in the organic phase decreases by decreasing nitric acid concentration within the limits of lower 1 mol/L. This tendency indicates that water is extracted differently between the cases of Fig. 3 and Fig. 5. In the case of Fig. 5, concentration of free-TBP, which is free from uranyl ions and nitric acid, is small and the hydrophobic property of normal dodecane appears to dominate the organic phase. Thus, water weakly bound with TBP is easily expelled. The similar phenomena is reported by Davis(9).

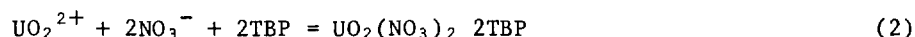
Tritium distribution ratio D_T is nearly constant in the present experimental range from 0.5 to 800 mCi/L of tritium concentration in the aqueous phase, as shown in Fig. 6. For this case, nitric acid concentration in the aqueous phase was 1.5 mol/L, uranium concentration in the

aqueous phase was 1.5 mol/L, uranium concentration in the organic phase was 85 g-U/L, and the temperature was 25 °C.

3. DISCUSSION

The present experiment indicated that tritium was extracted by tritiated water and nitric acid respectively. Extraction of water and nitric acid into organic solvents has been studied by many researchers (9-13). Estimation equations of the concentrations of uranium, nitric acid, and water in organic phase have been proposed and used in SEPHIS computer program(14) for the conditions of ordinary Purex process.

According to the literature, the following reactions occur during the present extraction. One mole of uranium is extracted as uranyl nitrate in co-ordination with two moles of TBP.



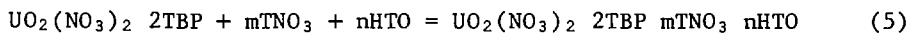
One mole of nitric acid is extracted in co-ordination with one mole of TBP within the concentration lower than 6 mol/L, which is the present experimental condition. Water is extracted in co-ordination with TBP by the ratio of n to one, where the value of n is smaller than unity. In the cases of tritiated water and tritiated nitric acid, these reactions are expressed by Eqs. (3) and (4).



Tritium reacts solely with free-TBP which is not co-ordinating with uranyl nitrate. In the literature(9), "free-TBP" has been defined as the TBP which is not co-ordinating both with uranyl nitrate and with nitric acid. However, this definition is unsuitable for the study of tritium scrubbing, since nitric acid is also tritiated. In the present work, therefore, free-TBP is defined as the TBP which is not co-ordinating solely with uranyl nitrate.

Relation between tritium distribution ratio and the free-TBP concentration is shown in Fig. 7 for the 30% TBP-nDD/uranyl nitrate-nitric acid-water system. Tritium distribution ratios D_T obtained for several nitric acid concentrations are plotted on the figure. The value of D_T is proportionate to the free-TBP concentration and nearly equals zero near zero

free-TBP concentration. This indicates that the tritium extracted by Eq. (5) is far smaller than that extracted by two reactions of Eqs. (3) and (4).



The lines in Fig. 7 represent the estimated distribution ratio of hydrogen atoms, which compose water and nitric acid, as a function of the free-TBP concentration. The equations proposed in SEPHIS program(14) were used in the present estimation of water and nitric acid concentrations in the organic phase. Equilibrium coefficient of uranyl nitrate K_U is expressed by

$$\begin{aligned} K_U &= \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]_{\text{org}}}{[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}} [\text{TBP}]_{\text{org}}^2} \\ &= (3.7n_a^{1.57} + 1.4n_a^{3.9} + 0.011n_a^{7.3})(4F^{-0.17} - 3)\exp(2,500T). \end{aligned} \quad (6)$$

Equilibrium coefficient of nitric acid K_H is

$$\begin{aligned} K_H &= \frac{[\text{HNO}_3 \cdot \text{TBP}]_{\text{org}}}{[\text{HNO}_3]_{\text{aq}} [\text{TBP}]_{\text{org}}} \\ &= (0.135n_a^{0.82} + 0.0052n_a^{3.44})[1.0 - 0.54\exp(-15F)]\exp(340T). \end{aligned} \quad (7)$$

where

$$n_a = [\text{HNO}_3]_{\text{aq}} + 2[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}} \quad (8)$$

$$T = \frac{1}{273 + t} - \frac{1}{298}. \quad (9)$$

Symbol F represents the TBP volume fraction in dry and solute-free solvent. The value of F is 0.3 for the present 30% TBP-nDD solvent, and temperature t is 20 °C. Molar water concentration in the organic phase $[\text{H}_2\text{O}]_{\text{org}}$ is expressed by

$$[\text{H}_2\text{O}]_{\text{org}} = (3.95 - 0.0144t) \left(1.0 - \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]_{\text{org}}}{U_{\text{os}}} - \frac{0.65[\text{HNO}_3 \cdot \text{TBP}]_{\text{org}}}{H_{\text{os}}} \right) F^{1.65} \quad (10)$$

where symbols U_{os} and H_{os} are molarities of uranium and nitric acid, respectively, required to saturate TBP in the organic phase. They are defined by

$$U_{os} = \frac{0.5 S}{1.0 + 0.046 S} \quad (11)$$

$$H_{os} = \frac{S[1.0 - 0.00609(3.95 - 0.0144t)F^{1.65}]}{1.0 + 0.043 S} \quad (12)$$

Symbol S represents molarity of TBP in dry and solute-free solvent, and the value of S is 1.096 mol/L for the present condition, which is indicated by the arrow mark on Fig. 7 showing the uranium-free system.

Molar concentrations of nitric acid $[\text{HNO}_3]_{\text{org}}$ and water $[\text{H}_2\text{O}]_{\text{org}}$ in the organic phase were calculated using these equations as a function of molar concentrations of nitric acid $[\text{HNO}_3]_{\text{aq}}$ and uranyl nitrate $[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}}$ in the aqueous phase. Concentration of hydrogen atoms in the organic phase was obtained by the values of $[\text{HNO}_3]_{\text{org}}$ and $[\text{H}_2\text{O}]_{\text{org}}$. Concentration of hydrogen atoms in the aqueous phase was obtained through the estimation of density. Density d_t (g/mL) of the aqueous phase at temperature t ($^\circ\text{C}$) was calculated by Eqs. (13) and (14) (ref. 15).

$$d_t = 1.0125d_{25} + 0.000145t - 0.00050td_{25} - 0.0036 \quad (13)$$

where d_{25} (g/mL) is the density at 25 $^\circ\text{C}$.

$$d_{25} = 1.10012 + 0.3177[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}} + 0.03096[\text{HNO}_3]_{\text{aq}} \quad (14)$$

Weight concentration of water in the aqueous phase was obtained by subtracting $[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}}$ and $[\text{HNO}_3]_{\text{aq}}$ from the value of d_t . Then, the concentration of hydrogen atoms was calculated from molar concentrations of water and nitric acid in the aqueous phase. The free-TBP concentration $[\text{TBP}]_{\text{org}}^f$ was calculated by

$$[\text{TBP}]_{\text{org}}^f = [\text{TBP}]_{\text{org}} - 2[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}} - 2[\text{TBP}]_{\text{org}} \quad (15)$$

The lines representing the distribution ratio of hydrogen atoms are shown in Fig. 7 as a function of the free-TBP concentration $[\text{TBP}]_{\text{org}}^f$ using nitric acid concentration $[\text{HNO}_3]_{\text{aq}}$ in the aqueous phase as a parameter. The distribution ratio of hydrogen atoms increases in proportion to the free-TBP concentration, and increases by increasing nitric acid concentration. The tritium distribution ratios D_T obtained in the present experiments, plotted on the figure, have the similar tendency to the estimated distribution ratio of hydrogen atoms. The tritium distribution ratios, however, generally give the smaller values than the estimated

distribution ratios of hydrogen atoms composing water and nitric acid.

Figure 8 shows distribution ratios for the case of 1 mol/L nitric acid concentration in the aqueous phase. The line represents the distribution ratio of hydrogen atoms calculated using by the estimation equations of nitric acid and water. Open circles represent the distribution ratios of hydrogen atoms calculated using the concentrations of nitric acid and water in the organic phase obtained in the present experiments. Solid dots are the tritium distribution ratios directly obtained in the present experiment. The open circles agree well with the line. This indicates that the distribution ratios of nitric acid and water obtained in the present experiment coincide with the estimation equations used. Solid dots, however, are slightly lower than the line. The discrepancy is considered to be caused by the isotope effect of tritium between the organic and aqueous phases. Then, isotopic distribution coefficient K_T of tritium between the phases was defined by the ratio of the isotopic concentration ratio $[T]/[H]$ in the organic phase to that in the aqueous phase.

$$K_T = \frac{([T]/[H])_{\text{org}}}{([T]/[H])_{\text{aq}}} \quad (16)$$

The values K_T obtained were plotted on Fig. 9 as a function of the free-TBP concentration for the cases of 3.5, 2.5, and 1.0 mol/L nitric acid concentrations in the aqueous phase. The mean value of K_T is found to be about 0.95, smaller than unity, although some scattering of the data is observed. The reciprocal equals to 1.05. The tritium isotope separation factor of water distillation method has been known to be the similar value (16). The isotope effect is caused by the different strength of the hydrogen bonding between the aqueous and vapor phases. In the present system, the strength of hydrogen bonding in the organic phase is weaker than that in the aqueous phase(17,18). Therefore, it may be concluded that tritium isotopic concentration in the aqueous phase is enriched by 1.05 times that in the organic phase.

4. CONCLUSION

For the purpose of establishing an effective tritium scrubbing technique in the fuel reprocessing process, tritium distribution ratios between the organic and aqueous phases were measured for the system of 30% TBP-nDD/uranyl nitrate-nitric acid-water. The following conclusions were obtained.

- (1) Tritium is extracted by TBP into the organic phase as both chemical species of tritiated water(HTO) and tritiated nitric acid(TNO₃).
- (2) Tritium distribution ratio decreases by increasing uranium concentration and increases by increasing nitric acid concentration, it does not vary along with tritium concentration in the present experimental condition.
- (3) Tritium distribution ratio ranges from 0.002 to 0.005 for the standard solution conditions of the Purex reprocessing process. Therefore, the value of tritium decontamination factor in the scrubbing step is expected in the range from 200 to 500 per one stage, if the stage efficiency is 100% in the process.
- (4) Isotopic distribution coefficient of tritium between the organic and aqueous phases was considered to be about 0.95.

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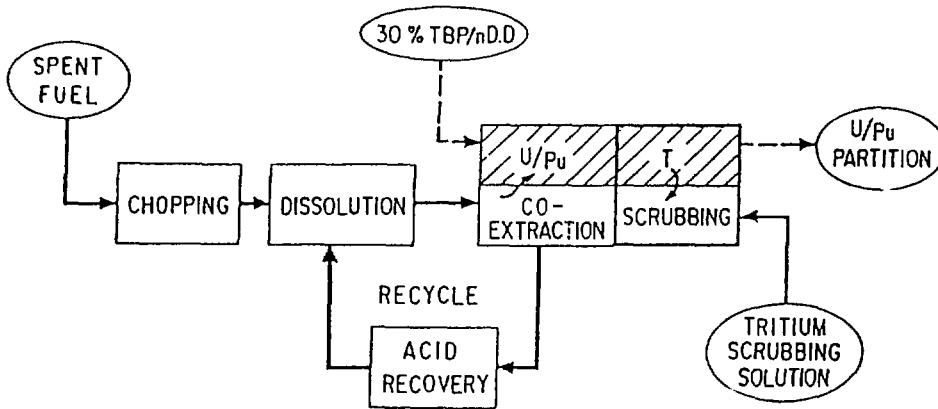


Fig. 1 A flow scheme of the tritiated water recycle process in nuclear fuel reprocessing.

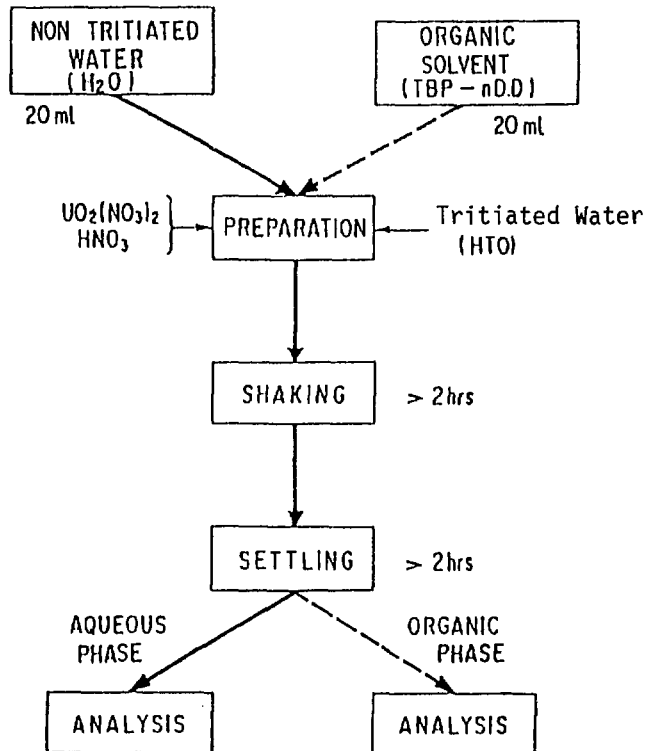


Fig. 2 Experimental procedure for measurement of tritium distribution ratio between the organic and aqueous phases.

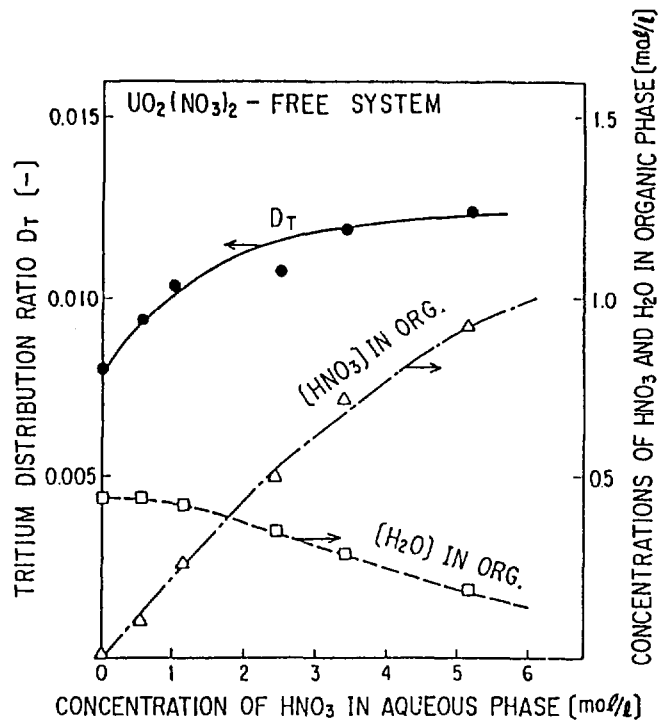


Fig. 3 Tritium distribution ratio, concentrations of nitric acid and water in a uranium-free 30% TBP-nDD organic phase, as a function of nitric acid concentration in the aqueous phase. The temperature is 20 °C.

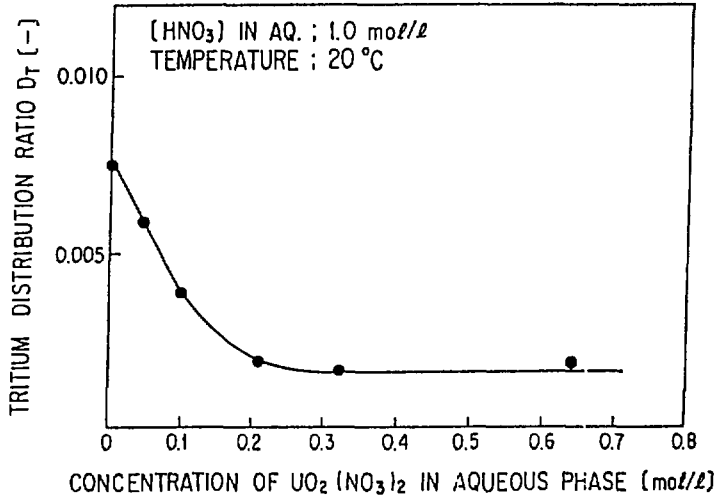


Fig. 4 Tritium distribution ratio as a function of uranyl nitrate concentration in the aqueous phase. Nitric acid concentration in the aqueous phase is constant at 1 mol/L and the temperature is 20 °C.

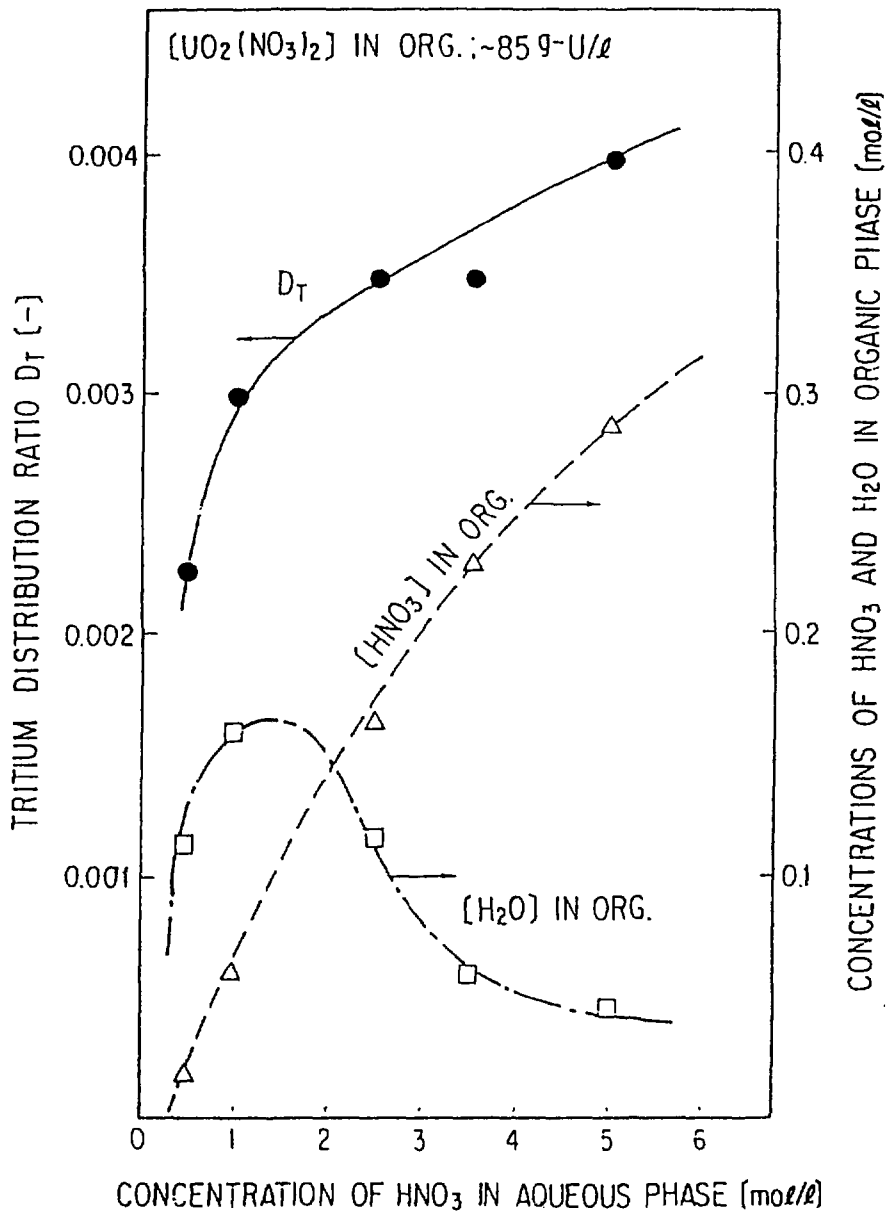


Fig. 5 Tritium distribution ratio, concentrations of nitric acid and water in a 30% TBP-nDD organic phase loaded uranyl nitrate of 85 g-U/L, as a function of nitric acid concentration in the aqueous phase. The temperature is 20 °C.

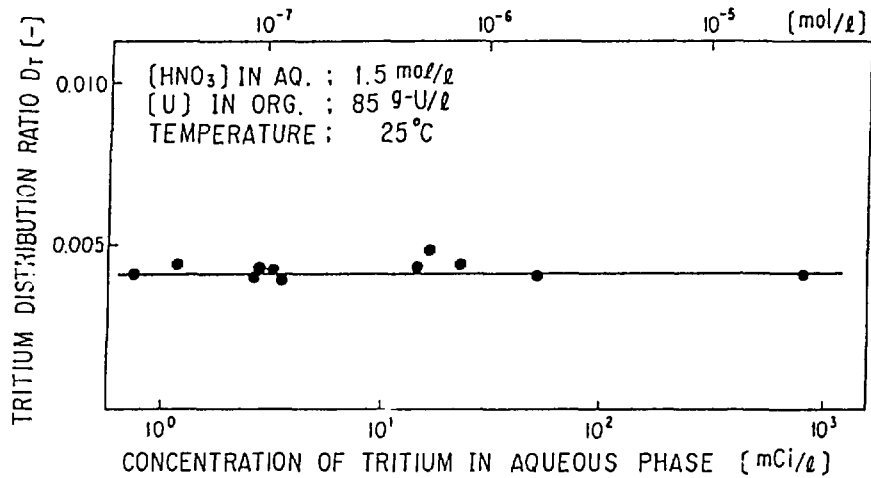


Fig. 6 Tritium distribution ratio as a function of tritium concentration in the aqueous phase. Nitric acid concentration is 1.5 mol/L in the aqueous phase, uranium concentration is 85 g-U/L in the organic phase, and the temperature is 25 °C.

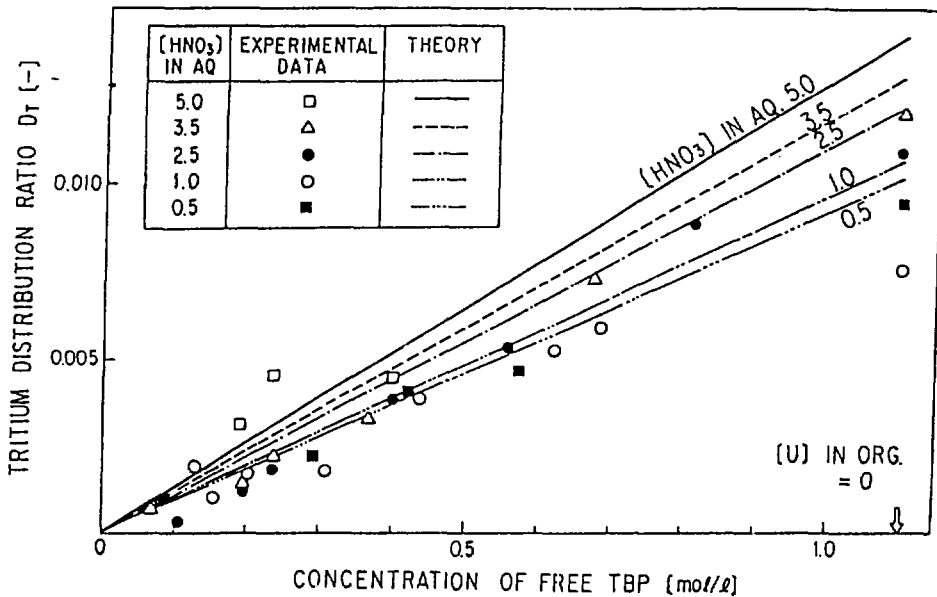


Fig. 7 Relation between tritium distribution ratio and the free-TBP concentration defined by Eq. (15), for a parameter of nitric acid concentration in the aqueous phase. The lines represent the estimated distribution ratio of hydrogen atoms composing water and nitric acid. The arrow mark shows the uranium-free condition.

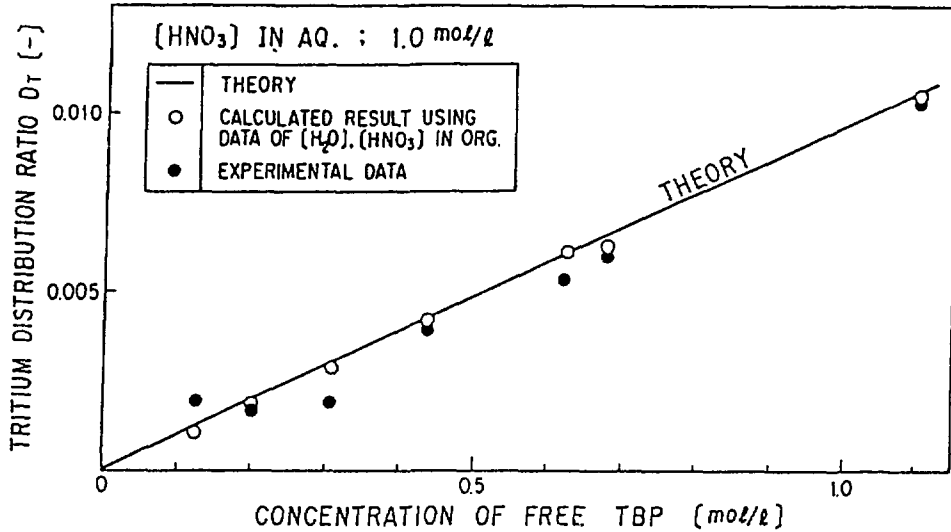


Fig. 8 Tritium distribution ratio as a function of the free-TBP concentration for the case of 1 mol/L nitric acid concentration in the aqueous phase. The line represents the distribution ratio of hydrogen atoms composing water and nitric acid.

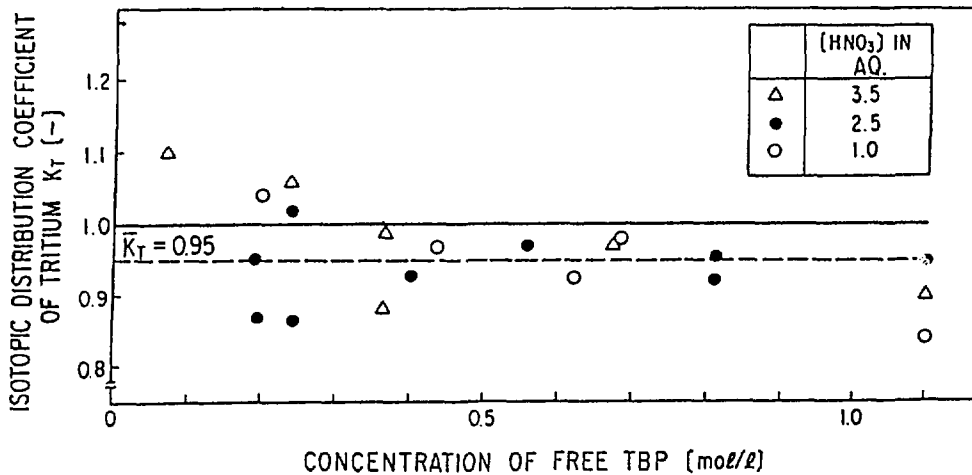


Fig. 9 Isotopic distribution coefficient of tritium defined by Eq. (16), as a function of the free-TBP concentration for the cases of 3.5, 2.5, and 1.0 mol/L nitric acid concentrations in the aqueous phase. The temperature is 20 °C.