

# Separation of Boron Isotopes in Extraction Systems Tetrafluoroboric Acid–Organophosphorus Compounds

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**Abstract**—Extraction systems based on extraction of tetrafluoroboric acid (HBF<sub>4</sub>) with tributyl phosphate (TBP) and triamylphosphine oxide (TAPO) for boron isotope separation were studied. Tetrafluoroboric acid was studied in comparison with boric acid (H<sub>3</sub>BO<sub>3</sub>). The extraction isotherms at 20°C for four systems (boric and tetrafluoroboric acids extracted with TBP and TAPO in *o*-xylene) were obtained, and single-stage isotope separation factors for these four systems were determined. The lighter boron isotope (<sup>10</sup>B) is concentrated in the aqueous phase in the systems containing tetrafluoroboric acid, whereas in the systems with boric acid it is concentrated in the organic phase.

**Keywords:** boron isotope separation, extraction, tetrafluoroboric acid boric acid, tributyl phosphate, triamylphosphine oxide

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## INTRODUCTION

Vigorous progress of such fields as nuclear power engineering, medicine, and instrument making makes it necessary to develop and produce specialty materials enriched in certain isotopes of various chemical elements. In particular, the boron isotope <sup>10</sup>B, which has high cross section of thermal neutron capture, is a valuable constituent of many materials. For example, materials based on <sup>10</sup>B are demanded in nuclear power engineering, namely, in reactor control and protection systems and in production of steel for transportation racks and containers for spent nuclear fuel (SNF). Boron-10 is used in neutron capture therapy for cancer treatment. High demand for materials enriched in <sup>10</sup>B and insufficient scale of their production make it topical to search for, study, and develop more efficient and environmentally safe procedures for boron isotope separation. Methods based on chemical isotope exchange, when isotope effects influence the properties of complexes of the extractive compound and extractant, are candidate separation methods. The “anisole process” is the most known and efficient among such methods. It is based on the reaction of gaseous BF<sub>3</sub> with anisole CH<sub>3</sub>OC<sub>6</sub>H<sub>5</sub> to form the complex CH<sub>3</sub>OC<sub>6</sub>H<sub>5</sub>·BF<sub>3(l)</sub>. This complex

interacts in countercurrent with BF<sub>3(g)</sub>, and isotope exchange occurs in the liquid–gas system with the <sup>10</sup>B accumulation in the liquid organic phase [1]. In such process, the enrichment factor  $\alpha$  reaches 1.030 [2].

An alternative procedure is liquid extraction. Extraction of boric acid was studied in some recent works [3, 4], but no studies were performed with tetrafluoroboric acid.

Organophosphorus compounds (OPCs) such as trialkyl phosphates and trialkylphosphine oxides can be used as extractants. Trialkyl phosphates are well known as effective extractants and are used for recovering many acids and salts, whereas trialkylphosphine oxides have been studied in this respect to a lesser extent, and their extracting and separating power is of large interest. To reach the maximum efficient isotope separation by liquid extraction in a multistep process, the substance distribution ratio should be as close to 1 as possible. The distribution ratio  $D$  is described by the equation

$$D = \frac{C_{\text{org}}^*}{C_{\text{aq}}^*},$$

where  $C_{\text{org}}^*$  is the equilibrium substance concentration in the organic phase, and  $C_{\text{aq}}^*$  is that in the aqueous phase.

Since the isotope separation in extraction systems directly depends on the difference between the constants of the transfer of substance isotopomers from the aqueous phase into the organic phase, it seems necessary to determine the factors directly influencing the substance distribution between the phases. Boron-containing substances that are well soluble in water and are extracted into the organic phase should be used as extractable substances. We consider boric acid  $\text{H}_3\text{BO}_3$  and tetrafluoroboric acid  $\text{HBF}_4$  as such substances. Boric acid as a weak acid cannot be efficiently extracted into the organic phase without additional complexation; therefore, tartaric acid is added to aqueous boric acid solutions. Tartaric acid converts boric acid into a complex that is a stronger acid interacting with the extractant more efficiently. Tetrafluoroboric acid does not require such additives.

It is interesting to consider organophosphorus compounds as extractants. Tributyl phosphate (TBP) is one of the most readily available and widely used commercial extractants. Along with TBP, mixed trialkylphosphine oxide Cyanex 923 is used for the recovery of metal ions. Despite their wide use for the extraction of metal cations, there are few data on extraction of boron-containing acids with them. Organophosphorus compounds (OPCs) were studied as extractants for acids structurally similar to  $\text{HBF}_4$ , i.e., for monobasic complex metal-containing acids  $\text{HMHal}_4$ , where M is a metal and Hal is a halogen. The data presented in review [5] show that compounds of metals in oxidation state (III) (such as Ga(III), In(III), Tl(III)) are extracted in the organic phase to form ion pairs consisting of solvated proton and metal-containing anion.  $\text{HBF}_4$  can be assumed to be extracted by OPCs by a similar mechanism. Mishra et al. [6] report the results of the extraction of  $\text{HFeCl}_4$  with tributyl phosphate ( $D = 3\text{--}8$ ) and mixed trialkylphosphine oxides Cyanex 921 and Cyanex 923 ( $D = 2\text{--}8$ ).

Khoroshilov and Ivanov [4] studied the boric acid–TBP extraction system in the context of separation of boron isotopes. They obtained the single-stage isotope separation factor  $\alpha = 1.0067 \pm 0.0035$  at  $20\text{--}22^\circ\text{C}$ . In this system,  $^{10}\text{B}$  was concentrated in the organic phase.

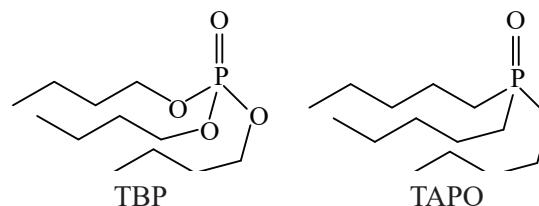
## EXPERIMENTAL

When recording the extraction isotherms of  $\text{H}_3\text{BO}_3$  and  $\text{HBF}_4$ , the boron concentrations in the equilibrium

phases were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) with a PlasmaQuant PQ9000 device at the Khlopin Radium Institute. Isotope analysis was performed by inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7900 device.

Samples for determining the boron isotope composition were prepared by dilution of the initial solutions of boron-containing components (boric and tetrafluoroboric acids) to a boron concentration of  $1\text{--}5\text{ mg/L}$ . In the case of tetrafluoroboric acid, it was subjected to hydrolysis in the presence of  $\text{CaCl}_2$  to remove fluoride ions interfering with the analysis.

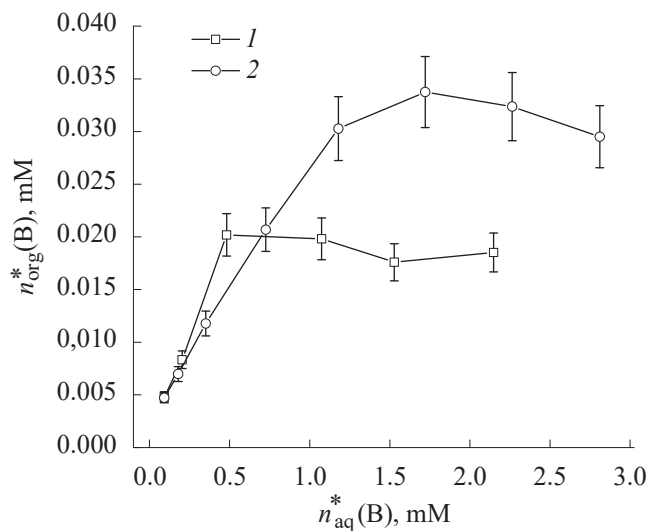
As organic diluent for the extractants we chose *o*-xylene, because this diluent prevents the third phase formation in extraction systems and favors fast phase separation, in contrast to aliphatic diluents such as dodecane. Prior to use, *o*-xylene was washed four times with equivalent amounts of distilled water. Chemically pure grade boric and tetrafluoroboric acids were used without additional purification. Tartaric acid was recrystallized from water and dried; the melting point after the purification was  $167^\circ\text{C}$ . Tributyl phosphate was purified as described in [7]. Triamylphosphine oxide (TAPO) chosen among trialkylphosphine oxides was purified as described in [8].



## RESULTS AND DISCUSSION

The extraction isotherms obtained for the  $\text{H}_3\text{BO}_3\cdot\text{C}_4\text{H}_9\text{O}_6\text{--TBP}$ ,  $\text{H}_3\text{BO}_3\cdot\text{C}_4\text{H}_9\text{O}_6\text{--TAPO}$ ,  $\text{HBF}_4\text{--TBP}$ , and  $\text{HBF}_4\text{--TAPO}$  systems (organic diluent: *o*-xylene) at  $20^\circ\text{C}$  are shown in Figs. 1 and 2.

We determined the distribution ratios for each extraction system. The highest distribution ratio  $D$  is reached in the  $\text{HBF}_4\text{--TAPO}$  system: 1.5 at low acid concentrations. High distribution ratio  $D$  is an advantage in commercial separation of boron isotopes, because at one extraction step the larger fraction of the substance is extracted, and thus the amount of the enriched product obtained increases.



**Fig. 1.** Isotherms of boric acid extraction with TBP and TAPO. (1) Extraction of  $H_3BO_3$  with 0.5 M TAPO in *o*-xylene, (2) Extraction of  $H_3BO_3$  with 1.5 M TBP in *o*-xylene.

The extraction mechanism in each system was determined from the shape of the extraction isotherm. In the  $H_3BO_3 \cdot C_4H_6O_6$ -TBP,  $H_3BO_3 \cdot C_4H_6O_6$ -TAPO, and  $HBF_4$ -TBP systems, the substance distribution is mainly physical. In the  $HBF_4$ -TAPO system, the extraction occurs by the chemical mechanism with the chemical interaction between  $HBF_4$  and TAPO. The chemical interaction between the system components is

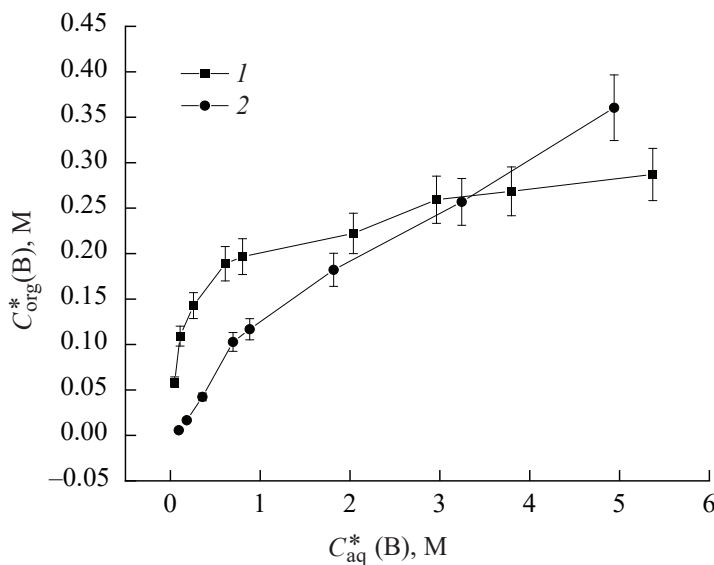
also an advantage for the extraction, because it increases the distribution ratio in the system.

We determined the single-stage isotope separation factors  $\alpha$  for the four extraction systems. The isotope separation in the systems with  $H_3BO_3$  is not so high, which may be due to a significant change in pH of the aqueous phase upon first contact and cessation of isotope separation in the second and further extractions. On the other hand, the enrichment in the systems with  $HBF_4$  is higher than in the systems with  $H_3BO_3$ .

Our data on the isotope separation in the  $H_3BO_3 \cdot C_4H_6O_6$ -TBP system can be compared to the data for the related system obtained in [4] (Table 1). The values coincide within the uncertainty.

The data obtained for all the four systems are given in Table 1.

Variation of the extractants influences the isotope separation not so strongly as the kind of the extractable substance does. The isotope separation factors in the  $HBF_4$ -TBP and  $HBF_4$ -TAPO systems are close and coincide within the uncertainty. The kind of the extractant influences to a greater extent the degree of extraction of the acid from the aqueous phase into the organic phase than the isotope effects. Studies of extraction isotherms have shown that the  $HBF_4$ -TAPO system gives the highest distribution ratio despite the



**Fig. 2.** Isotherms of tetrafluoroboric acid extraction with TBP and TAPO. (1) Extraction of  $HBF_4$  with 0.5 M TAPO in *o*-xylene, (2) extraction of  $HBF_4$  with 1.5 M TBP in *o*-xylene.

**Table 1.** Distribution ratios, compositions of extractable complexes, and isotope separation factors for the extraction systems under consideration

Extractable substance– extractant system	Distribution ratio $D$	Isotope separation factor $\alpha$
$\text{H}_3\text{BO}_3 \cdot \text{C}_4\text{H}_6\text{O}_6$ –TBP	0.05	$1.003 \pm 0.008$ ( $^{10}\text{B}$ is concentrated in organic phase) $1.0067 \pm 0.0035$ [4]
$\text{H}_3\text{BO}_3 \cdot \text{C}_4\text{H}_6\text{O}_6$ –TAPO	0.05	$1.001 \pm 0.011$ ( $^{10}\text{B}$ is concentrated in organic phase)
$\text{HBF}_4$ –TBP	0.15	$1.006 \pm 0.006$ ( $^{10}\text{B}$ is concentrated in aqueous phase)
$\text{HBF}_4$ –TAPO	1.5	$1.004 \pm 0.007$ ( $^{10}\text{B}$ is concentrated in aqueous phase)

fact that the TAPO concentration in the organic phase (0.5 M solution in *o*-xylene) in all the experiments was lower than the TBP concentration (1.5 M solution in *o*-xylene). Thus, the use of TAPO as an extractant is more advantageous from the viewpoint of the reagent consumption. As we found, in the extraction of  $\text{HBF}_4$ ,  $^{10}\text{B}$  is accumulated in the aqueous phase in contrast to the systems with  $\text{H}_3\text{BO}_3$ , in which  $^{10}\text{B}$  is concentrated in the organic phase.

Thus, it can be concluded that, among all the systems under consideration, the  $\text{HBF}_4$ –TAPO is the most suitable system for the boron isotope separation by liquid extraction, because this system is characterized by the highest distribution ratio  $D$ , the most efficient reagent consumption, and relatively efficient isotope separation at a single stage.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

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