Boron isotope separation by extraction method: features of the phase composition and flow reflux

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Abstract. The publication is devoted to comprehensive studies of boron isotope exchange in two-phase liquid-liquid systems and reflects the features of the extraction separation of boron isotopes, including reagent-free phase flow reflux. The achieved experimental values of the single stage enrichment factor are commensurate with the analogous values for the main production technologies of the 10B concentrating, and the reagent-free version of the flow reflux determines the competitiveness of such process. The method is considered an alternative to ion exchange and liquid chromatography, and, possibly, chemical exchange with the participation of boron trifluoride.

1. Introduction

In spite of hundreds of suggested methods for the boron isotope separation [1], their industrial production with a concentrating of $^{10}$B is implemented using only a few technologies based on two-phase vapor-liquid or gas-liquid systems [2-7]. These are (Figure 1) low-temperature distillation of boron trifluoride (170 K, $\alpha = 1.0075$) [2, 3], chemical exchange distillation of the complex compound BF$_3$ with dimethyl ether (370 K, $\alpha = 1.016$) [4-6] and chemical isotope exchange between boron trifluoride and its complex with methylphenyl ether (anisole) at a temperature (290 - 328) K when $\alpha = 1.026 - 1.030$ [7-10]. In this case, as can be seen, the greatest value of the separation factor of boron isotopes occurs during chemical isotope exchange.

**Main manufacturing processes for $^{10}$B and $^{11}$B**

- **Low Temperature Distillation** $\alpha = 1.0075$
- **Chemical Exchange Distillation** $\alpha = 1.016$
- **Chemical Exchange** $\alpha = 1.030$

Based on the use of boron trihalide BF$_3$

**Figure 1.** Main technological processes for the production of boron isotopes.
In all of these processes, the main working substance is boron trihalide (boron trifluoride). The advantage of the listed processes is that there is no need to use reagents to the flow reflux, since these processes are carried out thermally: due to the evaporation and condensation of the substance during the distillation or due to the thermal dissociation of the D-BF₃ complex or its formation during heat removal. One of the main disadvantages of these processes is the high danger of working with BF₃ and its compounds (complexes). This leads to significant additional costs, which, of course, affects the cost of isotope production.

An alternative to boron trifluoride could be another working substance - safe boric acid (Figure 2). For example, in the form of such a process as ion exchange, that is, chemical isotope exchange in a liquid - solid system [11-13]. The exchange takes place in this case between boric acid in water and tetraborate anion in an ion exchange resin. The process is carried out in mass transfer columns, for example, in the Spedding’s zone mode [14]. The main disadvantage of this process is the chemical flow reflux using not cheap reagents - alkali and acid. There are examples when the established ion-exchange isotope production stopped working due to poor economics.

One more drawback of the ion-exchange method should be noted – the relatively low throughput of the ion-exchange resin and, accordingly, the large diameter of the mass-exchange columns.

The transition to isotope exchange with boric acid in the liquid - liquid systems could become a more promising process for the separation of boron isotopes.

This process can be carried out in a cascade of centrifugal extractors placed on a horizontal surface. By analogy with the ion exchange process, the method of boron isotopes separation in a liquid-liquid system can be called an extraction process [15, 16]. The main task in the implementation of this method is to select a working system that allows you to implement a reagent-free method for the flows reflux, that is, to carry out the processes of extraction and re-extraction of boron.

This publication is devoted to the results of such studies.

2. Experimental part: methods, results and discussion

2.1 Phase and isotopic equilibrium

In experimental studies, aqueous and organic solutions of different concentrations were prepared. The solutions were in contact with each other for a certain time, after which samples of each of the phases were taken for further elemental and isotopic analysis. We described in detail the methodological features of the research earlier [16-18], where the obtained experimental results were also partially presented.
To develop such a process with the participation of boric acid, a number of liquid-liquid systems have been studied with the determination of the distribution ratio of boron between the phases, measurement of the single isotope effect and, in some cases, with the study of the possibility of reagent-free flow reflux.

The Table 1 provides brief information for the five systems we studied, where the organic phase was either tributyl phosphate (TBP) - system number one, or a secondary amine, both in a solvent (system 2) and without it (systems three and four). As for boric acid, its concentration in the initial aqueous solution varied from a tenth of a mole to almost the limit of its solubility in water at room temperature.

Table 1. Liquid-liquid systems and their main properties

| №  | Liquid-liquid system                                                                 | Boric acid concentration $C_\text{aq}$, M | Distribution ratio $D$   | Single stage separation factor $\alpha$ | Note                  |
|----|-------------------------------------------------------------------------------------|-------------------------------------------|--------------------------|----------------------------------------|------------------------|
| 1  | B(OH)$_3$, aq - B(OH)$_3$ in 100% TBP, org                                          | $0.2 - 0.75$                              | $\approx 0.2$            | $1.005 - 1.007$                        | phase isotope effect   |
| 2  | B(OH)$_3$, aq - 0.5 M diethylamine (DEA) in xylene, org                             | 0.5                                       | 0.001704 ± 0.000030     | 1.0112$^2$                            | isotope effect inversion |
| 3  | B(OH)$_3$, aq - dipropylamine (DPA), org                                             | 0.1 - 0.6                                 | 0.0151 - 0.0069         | (1.022 - 1.031)$^2$                   |                        |
| 4  | B(OH)$_3$, aq - dibutylamine (DBA), org                                              | 0.1 - 0.75                                | 0.117 - 0.159           | (1.020 - 1.025)$^2$                   |                        |
| 5  | B(OH)$_3$, aq + TA$_3$, aq - trioctylamine (TOA) in xylene, org                      | $0.07 - 0.75$                             | 1.9 - 120               | 1.015 - 1.040                         |                        |

Notes: $^1$ - tributyl phosphate (C$_{4}$H$_9$O$_3$)PO; $^2$ - $^{10}$B concentrates in the aqueous phase; $^3$ - tartaric acid.

In the four listed in Table 1 cases, the measured values of the distribution ratio are small: from a few hundredths to tenths of a mole. The results of measurements of the separation (enrichment) factor for boron isotopes are very interesting. For the system with tributyl phosphate, the value of this parameter is relatively small and, most likely, reflects the so-called phase isotope effect. In this case, boron-10 is concentrated in the organic phase, as is the case in almost all known cases.

A different direction of boron-10 concentration is characterized by systems with secondary amines, in which this isotope is concentrated in the aqueous phase, that is, there is an inversion in the direction of the isotope effect. Moreover, the values of epsilon (themselves as alpha minus one) are two to five times greater. This suggests that in such systems processes of chemical isotope exchange occur, and the alpha inversion is due to the effect of the solubility of secondary amines in water.

The most interesting results were obtained by us when studying a system with a tertiary amine, namely, with trioctylamine. This amine was chosen by us in contrast to secondary amines from the point of view of solubility in water. But boric acid is practically not extracted with pure TOA, so it was necessary to use a “transport reagent”, which is hydroxycarboxylic acids. Having studied a number of such acids (malic, citric, tartaric), we based on the use of tartaric acid, which was added to an aqueous solution of boric acid. For this system, as can be seen, the distribution ratio has very high values. At the same time, the isotope effect is also high here, with boron-10 being concentrated in the organic phase. Of course, the properties of such a system should be considered more carefully (Table 2).
With an increase in the initial concentration of boric acid, the distribution ratio decreases. In the region of relatively high boric acid concentration, that is, in the practically interesting region, the D values are in the range 1.9 - 7.8. Under the separation of boron isotopes the distribution ratio in phases should be 1:1. This means that when D is more than unity, it will be necessary to reduce the flow of the organic phase.

It is interesting to consider the effect of the initial boric acid concentration on the distribution ratio. This type of dependence (Figure 3) most likely indicates the formation of associates in the organic phase.

**Table 2.** Phase equilibrium in the system “Aqueous solution of boric and 0.5 M tartaric acids - TOA in o-xylene” at a concentration of 0.5 M TOA in o-xylene

| Initial aqueous solution | Equilibrium aqueous phase | Equilibrium organic phase | Distribution ratio D |
|--------------------------|----------------------------|---------------------------|---------------------|
| $C_{\text{aq}}$, M       | pH                         | $C_{\text{aq}}$, M        | $C_{\text{org}}$, M |
| 0.070 ± 0.001            | 1.30 ± 0.05                | 0.0006 ± 0.0001           | 1.87 ± 0.05         |
| 0.150 ± 0.002            | 1.11 ± 0.05                | 0.003 ± 0.001             | 2.00 ± 0.05         |
| 0.300 ± 0.004            | 0.98 ± 0.05                | 0.005 ± 0.003             | 2.12 ± 0.05         |
| 0.400 ± 0.006            | 0.94 ± 0.05                | 0.014 ± 0.003             | 2.22 ± 0.05         |
| 0.500 ± 0.007            | 0.91 ± 0.05                | 0.06 ± 0.01               | 2.32 ± 0.05         |
| 0.600 ± 0.008            | 0.85 ± 0.05                | 0.126 ± 0.009             | 2.32 ± 0.05         |
| 0.75 ± 0.01              | 0.81 ± 0.05                | 0.26 ± 0.01               | 2.23 ± 0.05         |

**Figure 3.** Distribution ratio $D$ in the system “Aqueous solution of boric and 0.5 M tartaric acids - TOA in o-xylene” at a concentration of 0.5 M TOA in o-xylene

Particularly interesting is the question of the separation (enrichment) single stage factor. To determine the effect of the system composition on the enrichment factor, several series of experiments were carried out. On the whole, a large amount of experimental material has been obtained. Here are the main results (Table 3).

**Table 3.** Single stage enrichment factor of boron isotopes in liquid-liquid system $\text{B(OH} \text{)}_3, \text{aq} + \text{TA, aq} - \text{TOA in xylene, org}$

| Boric acid concentration in water $C_{\text{BA, M}}$ | TA concentration in water $C_{\text{TA, M}}$ | TOA concentration in xylene $C_{\text{TOA, M}}$ | Single stage enrichment factor $\varepsilon = \alpha - 1$ |
|--------------------------------------------------|---------------------------------------------|-----------------------------------------------|------------------------------------------------------|
| 0.300$_0$ ± 0.001$_6$                             | 0.500$_0$ ± 0.0008$_3$                      | 5.000$_0$ ± 0.002$_6$                         | 0.018$_0$ ± 0.003$_3$                                  |
| 0.500$_0$ ± 0.001$_7$                             |                                            |                                               | 0.025$_0$ ± 0.003$_7$                                  |
| 0.750$_0$ ± 0.001$_0$                             |                                            |                                               | 0.033$_0$ ± 0.003$_0$                                  |

Studied the influence of the concentration of boric and tartaric acids, as well as the concentration trioctylamine. In general, enrichment factor ($\varepsilon = \alpha - 1$) is shown to vary over a wide range of
values: from 0.015 to 0.040. With an increase in the initial concentration of boric acid, enrichment factor monotonic increases. With an increase in the concentration of tartaric acid (Figure 4), the $\varepsilon$ dependence passes through a maximum (when the initial concentrations of all three components are equal). An increase in the TOA concentration up to 1 M (Figure 5) leads to an increase in the epsilon maximum value at the indicated concentration.

Figure 4. The influence of the concentration of tartaric acid in the system $\text{B(OH)}_3, \text{aq} + \text{TA, aq} - \text{TOA in xylene} \text{,org}$ on the enrichment factor of boron isotopes.

Figure 5. The influence of the concentration of trioctylamine in the system $\text{B(OH)}_3, \text{aq} + \text{TA, aq} - \text{TOA in xylene} \text{,org}$ on the enrichment factor of boron isotopes.

At average concentrations of components (0.5 M boric acid, 0.5 M tartaric acid, 0.5 M TOA) single stage enrichment factor is $\varepsilon = 0.025$. The studies performed make it possible to determine the optimal composition of a two-phase system from a practical point of view. The processes occurring in the studied two-phase system can be divided into two stages (Figure 6). In the first stage the presence of tartaric acid in water phase leads to the formation of an amino complex compound with boric acid in the organic phase. This acid plays the role of a carrier of boric acid. Further, an isotope exchange reaction occurs between boric acid in the aqueous phase and the amino complex in the organic phase, as a result of which boron-10 is concentrated in the amino complex.

Figure 6. General view of the boron isotope exchange mechanism in the system $\text{B(OH)}_3, \text{aq} + \text{TA, aq} - \text{TOA in xylene} \text{,org}$.
2.2 The overall scheme of the process and flow reflux

To organize the process of boron isotopes concentrating, it is necessary to multiply the single stage separation effect. For this, it is necessary to organize a flow reflux, which is not always possible to do in practice. Flow reflux, is a quantitative transfer of an element, the isotopes of which separate (in the considered case of boron) from one phase to another. Since boron-10 is concentrated in the organic phase in the system under study, boron should be transferred from this phase to the aqueous phase, that is, re-extraction should be performed (Figure 7). In this case, the main task is to avoid the use of reagents, that is, to create a reagent-free process.

![Diagram of the separation process](image)

**Figure 7.** General scheme of the separation process in B(OH)₃ or BAₐq + TAₐq - TOA (RN) in xylene.\(\text{org}\) system (for boron-10 concentration problem).

From the point of view of the concentration of boron-11, the formation of the amine complex proceeds easily (amine complex formation unit). As you can see from the Table 4, 85% of the boric acid passes into the organic phase.

**Table 4.** Investigation of flow reflux for \(^{11}\text{B} \) (0.5 M TA, 0.5 M TOA in xylene)

| Initial aqueous phase \(C_{\text{aq}}^0\), M | Equilibrium aqueous phase \(C_{\text{aq}}^*\), M | Equilibrium organic phase \(C_{\text{org}}^*\), M | Distribution ratio \(D\) |
|---------------------------------|---------------------------------|---------------------------------|------------------|
| 0.508 ± 0.004                  | 0.0707 ± 0.0007                 | 0.429 ± 0.004                  | 6.07 ± 0.08      |

The most important, based on the diagram in the figure 7, is the flow reflux in the area of maximum concentration of \(^{10}\text{B}\). When studying the flow reflux for boron-10, we performed a large number of experiments. Shown here are a number of results that demonstrate reagent-free flow reflux. Regardless of the concentration of boric acid in organic matter, the Boron recovery rate was 99.6 percent at the use of distilled water (Table 5).

**Table 5.** Investigation of flow reflux for \(^{10}\text{B} \) (0.5 M TA, 0.5 M TOA in xylene)

| Initial organic phase \(C_{\text{org}}^0\), M | Equilibrium aqueous phase \(C_{\text{aq}}^*\), M | Equilibrium organic phase \(C_{\text{org}}^*\), M | Boron recovery rate, % |
|---------------------------------|---------------------------------|---------------------------------|----------------------|
| 0.429 ± 0.004                  | 0.0395 ± 0.0002                 | 0.0017 ± 0.0002                 | 99.6                 |

An increase in the temperature of the boric acid re-extraction process, as well as the use of other additional techniques, makes it possible to obtain a residual boron concentration in the organic phase at the level of (2 - 3) ppm, which makes it possible to obtain boron-10 with a
concentration of about 60 at.%. The results obtained allow us to say that the proposed method for separation of boron isotopes allows, if necessary, to obtain a more concentrated isotope $^{10}\text{B}$, using chemical flow reflux while reducing the consumption of reagents by about 250 times.

**Conclusion**

The use of boric acid as a working substance reduces the risk of production and reduces the cost of raw materials and labor protection.

The value of the separation factor is practically equal to $\alpha$ for a known industrial method - anisole method.

Flow reflux in the first approximation allows concentrating $^{10}\text{B}$ up to 60 % at. by reagent-free way or reduce the consumption of reagents by about 250 times at production of $^{10}\text{B}$ with more concentration.

The use of centrifugal extractors in the separation cascade will make it possible to create the production of boron isotopes of the horizontal type.

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