Inversion of boron isotope effect during chemical exchange in extraction systems

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Abstract. In the processes of boron isotopic exchange in liquid-liquid systems using boric acid as the main working substance, the lighter boron isotope is concentrating in the organic phase, which takes place both in the case of phase exchange (tributyl phosphate, TBP) and at the chemical (trioctylamine, TOA) isotope exchange. That is, boron-10, as a rule, predominantly passes into the organic phase. In contrast to the previously observed effects, our studies for several extraction systems using secondary amines (diethyl, dipropyl, and dibutylamine as the organic phase) demonstrated the inversion of the boron isotope effect when a more light isotope $^{10}$B is concentrated in the aqueous phase. At the same time, the level of the values of the single stage separation factor of boron isotopes turned out to be quite high and amounted to 1.020 - 1.028. The paper discusses the possible causes of the discovered phenomenon, and also considers the potential for practical application of such an effect.

1. Introduction

The first study of boron isotope separation by extraction was performed in the early 1960s in the system “aqueous solution $\text{H}_3\text{BO}_3$ – isoamyl alcohol” [1], for which the single stage separation factor of boron isotopes was $\alpha = 1.0027$. Higher values of $\alpha$ were obtained by extraction of boric acid by 1,1,7-trihydrododecafluoroheptanol [2]: as the authors indicate, $\alpha$ was found to be not larger than 1.005.

In a previous work [3], we examined extraction systems using tributyl phosphate (TBP) and trioctylamine (TOA) in xylene as the organic phase. It was found that the single stage separation factor of boron isotopes for a system using TBP is approximately 1.0067, and for a system using TOA in xylene approximately 1.025.

In all cases, the separation of boron isotopes occurred in such a way that boron-10 was mainly concentrated in the organic phase. Based on the results we obtained earlier, we can conclude that the use of amines for the separation of boron isotopes in liquid-liquid systems may be most appropriate in view of the magnitude of the single stage separation factor.
It is possible that the use of other amines as extractants can lead to the formation of a boric acid complex in the organic phase, with the participation of which the isotope enrichment coefficient $\alpha = \varepsilon - 1$ will be no less than in a system with TOA.

The results of experimental studies of phase equilibrium and measurement of a single stage separation factor for boron isotopes in three extraction systems are considered in the article: system 1 - aqueous solution of boric acid – 0.5 M diethylamine (DEA) in xylene; system 2 - aqueous solution of boric acid – dipropylamine (DPA); system 3 - aqueous solution of boric acid – dibutylamine (DBA).

2. **Method of extraction and analysis**

2.1. **Experimental method for the extraction of boron**

Boric acid extraction was carried out from the $\text{H}_3\text{BO}_3$ aqueous solution by an organic liquid (in the presence or absence of a solvent). If the solvent was required in the organic phase, the required volume of extractant was diluted and brought to a certain volume by the solvent (o-xylene) to obtain the required concentration of extractant in the organic phase. Extraction was carried out at room temperature in separatory funnels at different volume ratio of the organic and aqueous phases (org:aq or aq:org). Also in the experiments, the initial concentration of boric acid $C_{\text{aq}}^0$ varied over a wide range of values. After the separation funnel was filled with aqueous and organic phases, its contents were vigorously stirred and held until complete phase separation, after which the phases were successively poured into separate containers. Then, the pH value was determined in the aqueous phase, and the concentration of boron was determined in the aqueous ($C_{\text{aq}}^*$) and organic ($C_{\text{org}}^*$) phases.

Further, an isotopic analysis was carried out for the aqueous and organic phases to determine the isotopic ratio of boron in the aqueous and organic phases.

2.2. **Quantitative analysis of boron in aqueous and organic phases**

The quantitative determination of boron in the aqueous and organic phases was carried out by the ICP-MS method on the mass-spectrometer XSeriesII (Thermo Scientific) in peak jumping mode using the multi-element standard ISP-MS-68 Solution A (High-purity Standards). In this case, samples of the aqueous and organic phases were preliminarily mixed with highly pure nitric acid to remove the matrix effect due to the presence of secondary amines in the samples. After that, the samples were diluted with freshly prepared double-distilled water and analysis was carried out.

2.3. **Isotope analysis**

Isotope analysis of boron in boric acid both in initial aqueous and in equilibrated aqueous and organic phases was carried out by ICP-MS method on the mass-spectrometer XSeriesII (Thermo Scientific) relative to the isotope boron standard SRM 951 according to the previously developed method [4].

The boron isotope ratio was measured in peak jumping mode in high resolution. Preliminary dilution of the samples was carried out to a boron concentration of 100 ppb, which simultaneously gave a high value of the number of pulses for the analyzed isotopes and an insignificant memory effect of the mass spectrometer during the analysis. The sequence of analysis of each sample included the following stages: measuring the background signal, measuring the standard sample, washing with double-distilled water, measuring the background signal, measuring the sample, washing with double-distilled water, measuring the background signal, measuring the standard sample. Each measurement was repeated five times. By measuring the standard sample before and after measuring the sample, a correction factor was determined taking into account the effect of mass discrimination.

3. **Results and discussion**

3.1. **Phase equilibrium**

As a result of studying the phase equilibrium for systems 2 and 3, extraction isotherms were obtained (figure 1). Since diethylamine mixes unlimitedly with water, xylene was used as a solvent of the
organic phase to keep the system in a two-phase state. However, for system 1, it was possible to reliably obtain only one point of phase equilibrium of boron, which indicates that diethylamine practically does not extract boric acid from its aqueous solution.

For system 1, the numerical value of the extraction coefficient $K_D$ does not exceed 0.002, which is 100 times less than the value of the extraction coefficient when using TBP [3]. The obtained value and properties of diethylamine indicate the unpromising use of system 1 for the separation of boron isotopes.

For systems 2 and 3, according to the obtained isotherms of boron extraction, it can be seen that the extraction coefficient $K_D$ is significantly larger than for system 1, but still its value is less than 1. For system 2 and 3, the values of the extraction coefficient from the initial concentration of boric acid (in the range from 0.1 M to 0.75 M) will be described by equations (1) and (2), respectively:

$$K_D = -0.1456 \times (C_{aq}^\ast)^2 + 0.2131 \times C_{aq}^\ast - 0.0057$$

(1)

$$K_D = -0.4601 \times (C_{aq}^\ast)^2 + 0.4081 \times C_{aq}^\ast + 0.0692$$

(2)

From the point of view of pH values of the equilibrium aqueous phase, several ionic forms of the boric acid molecule can be distinguished (table 1) with a different ratio of three- $[\text{BO}_3]$ and four- $[\text{BO}_4]$ coordinated boron [5, 6]. The conversion of boric acid into the forms indicated in table 1 is carried out in view of the partial dissolution and hydrolysis of secondary amines in the aqueous phase and is described by equations (3), (4), (5) and (6):

$$\text{R}_2\text{NH} + \text{HOH} \leftrightarrow [\text{R}_2\text{NH}_2] [\text{OH}]^-$$

(3)

$$\text{B(OH)}_3 + \text{OH}^- \leftrightarrow \text{B(OH)}_4^-$$

(4)

$$3\text{B(OH)}_3 + \text{OH}^- \leftrightarrow \text{B}_3\text{O}_5(\text{OH})_4$$

(5)

$$3\text{B(OH)}_3 + 2\text{OH}^- \leftrightarrow \text{B}_3\text{O}_5(\text{OH})_5^2^-$$

(6)
### Table 1. Forms of boric acid in equilibrium aqueous phase

|           | $w$ - form | $x$ - form | $y$ - form | $z$ - form |
|-----------|------------|------------|------------|------------|
| B(OH)$_3$ | B(OH)$_4^-$ | B$_3$O$_3$(OH)$_4^-$ | B$_3$O$_3$(OH)$_5^{2-}$ |

![Diagram of boric acid forms]

$[\text{BO}_4^2^- : \text{BO}_3^- ] = 0:1$

$[\text{BO}_4^2^- : \text{BO}_3^- ] = 1:0$

$[\text{BO}_4^2^- : \text{BO}_3^- ] = 1:2$

$[\text{BO}_4^2^- : \text{BO}_3^- ] = 2:1$

The pH value of the equilibrium aqueous phase, the molar fraction of the forms of boric acid and the extraction coefficient $K_D$ are shown in Table 2.

### Table 2. Characteristics of the equilibrium aqueous phase and the extraction coefficient $K_D$

| System 1 | The molar fraction of boron in the aqueous phase | $K_D$ |
|----------|-----------------------------------------------|-------|
|          | $w$ - form | $x$ - form | $y$ - form | $z$ - form |       |
| pH = 10.23 | 0.998154 | 0.000902 | 0.000944 | 2.5·10^{-7} | 0.001708 ± 0.000030 |

| System 2 | The molar fraction of boron in the aqueous phase | $K_D$ |
|----------|-----------------------------------------------|-------|
|          | $w$ - form | $x$ - form | $y$ - form | $z$ - form |       |
| pH = 11.59 | 0.979066 | 0.019935 | 0.000993 | 6.0·10^{-6} | 0.01511 ± 0.00084 |
| pH = 11.31 | 0.987441 | 0.010503 | 0.002049 | 6.5·10^{-6} | 0.0309 ± 0.0012 |
| pH = 11.16 | 0.989063 | 0.007517 | 0.003413 | 7.8·10^{-6} | 0.0466 ± 0.0012 |
| pH = 11.04 | 0.991035 | 0.005661 | 0.003298 | 5.6·10^{-6} | 0.0534 ± 0.0023 |
| pH = 10.94 | 0.990916 | 0.004496 | 0.004582 | 6.2·10^{-6} | 0.0673 ± 0.0018 |
| pH = 10.87 | 0.990147 | 0.003868 | 0.005978 | 7.0·10^{-6} | 0.0687 ± 0.0028 |

| System 3 | The molar fraction of boron in the aqueous phase | $K_D$ |
|----------|-----------------------------------------------|-------|
|          | $w$ - form | $x$ - form | $y$ - form | $z$ - form |       |
| pH = 10.18 | 0.999094 | 0.000797 | 0.000109 | 2.6·10^{-8} | 0.1312 ± 0.0055 |
| pH = 10.02 | 0.999196 | 0.000551 | 0.000253 | 4.2·10^{-8} | 0.1588 ± 0.0053 |
| pH = 9.95 | 0.999183 | 0.000469 | 0.000348 | 4.9·10^{-8} | 0.1569 ± 0.0062 |
| pH = 9.86 | 0.999163 | 0.000381 | 0.000455 | 5.2·10^{-8} | 0.1471 ± 0.0039 |
| pH = 9.79 | 0.999060 | 0.000325 | 0.000616 | 6.0·10^{-8} | 0.1174 ± 0.0013 |

3.2. The values of the single isotope effect and the distribution mechanism between the aqueous and organic phases

To determine the value of a single isotope effect in systems 1, 2 and 3, the values of the isotope ratio $R$ of the aqueous phase and the organic phase after equilibration was determined. Isotope ratio $R$ is the ratio of isotope concentrations of boron-11 to boron-10, which looks like equation (7):
In this case, taking into account the isotope ratio for SRM 951 ($R^{st}$), the true value of the isotope ratio is determined by equation (8):

$$R_{true}^* = R_{measured}^* \times \frac{R_{true}^{st}}{R_{measured}^{st}}$$ (8)

According to the results of measurements of the ratio of isotopes in systems 1, 2 and 3, it was found that during the extraction of boric acid $^{10}\text{B}$ is concentrated in the aqueous phase, and the isotope $^{11}\text{B}$, respectively, in the organic phase. This is opposite to the previously considered isotopic effects of boron in extraction systems and is determined by the obtained pH values of the equilibrium aqueous phase. In accordance with the above, to express the value of the isotope effect so that its value is greater than 1, the equation (9) for calculating a single stage isotope effect:

$$\alpha = \frac{R_{aq}^{10} \times R_{org}^{11}}{R_{aq}^{11} \times R_{org}^{10}} = R_{aq}^*$$ (9)

Table 3 presents data on the value of a single stage separation factor of boron isotopes depending on the pH value of the equilibrium aqueous phase and boron concentrations in the equilibrium aqueous and organic phases.

**Table 3. Values of a single stage separation factor of boron isotopes for systems 1, 2, and 3.**

| System 1 | $C_{aq}$, М | $C_{org}$, М | pH | $\alpha$ |
|----------|---------------|---------------|----|----------|
|          | $0.4992 \pm 0.0057$ | $0.000853 \pm 0.000011$ | 10.23 | $\sim 1.0112$ |
| System 2 | $C_{aq}$, М | $C_{org}$, М | pH | $\alpha$ |
|          | $0.1110 \pm 0.0035$ | $0.001677 \pm 0.000077$ | 11.59 | $1.0254 \pm 0.0013$ |
|          | $0.2178 \pm 0.0073$ | $0.00672 \pm 0.00012$ | 11.31 | $1.0270 \pm 0.0013$ |
|          | $0.3317 \pm 0.0046$ | $0.01545 \pm 0.00032$ | 11.16 | $1.0312 \pm 0.0013$ |
|          | $0.375 \pm 0.010$ | $0.02004 \pm 0.00069$ | 11.04 | $1.0274 \pm 0.0013$ |
|          | $0.496 \pm 0.012$ | $0.03339 \pm 0.00036$ | 10.94 | $1.0220 \pm 0.0013$ |
|          | $0.6113 \pm 0.0080$ | $0.0420 \pm 0.0016$ | 10.87 | $1.0225 \pm 0.0013$ |
| System 3 | $C_{aq}$, М | $C_{org}$, М | pH | $\alpha$ |
|          | $0.1799 \pm 0.0045$ | $0.02360 \pm 0.00080$ | 10.18 | $1.0232 \pm 0.0013$ |
|          | $0.330 \pm 0.011$ | $0.05241 \pm 0.00016$ | 10.02 | $1.0251 \pm 0.0013$ |
|          | $0.4195 \pm 0.0050$ | $0.0658 \pm 0.0025$ | 9.95 | $1.0231 \pm 0.0013$ |
|          | $0.5324 \pm 0.0053$ | $0.0783 \pm 0.0019$ | 9.86 | $1.0215 \pm 0.0013$ |
|          | $0.6712 \pm 0.0052$ | $0.07880 \pm 0.00061$ | 9.79 | $1.0196 \pm 0.0013$ |

According to the data in table 3, the similarity of the values of the single stage separation factor of systems 2 and 3 with the system using TOA [3] is noticeable (taking into account the expression of $\alpha$ so that its value is greater than 1).

Considering that for systems with secondary amines an extraction coefficient $K_D$ of less than 1 was obtained, the presence of various forms of boric acid in the equilibrium aqueous phase, the concentration of the boron-10 isotope in the aqueous phase, and data on the formation of the boric acid and DBA compound, which corresponds to the $\gamma$- form of boric acid [7], we can describe the process of separation of boron isotopes in the systems under consideration by the following mechanism:
1. Partial dissolution and hydrolysis of the secondary amine in the aqueous phase;
2. The formation in the aqueous phase of the $x$, $y$- and $z$- forms of boric acid with the establishment of isotopic equilibrium between these forms and the $w$- form;
3. The distribution of the secondary amine compound with the $y$- form of boric acid, that is, the extraction of this compound into the organic phase due to its partial dissolution in the organic phase.

Given equations (4), (5) and (6), we can express the integral equation (10) of the isotopic exchange of boron between three- and four-coordinated states. In this case, the general mechanism of the distribution of the forms of boric acid (figure 2) between the aqueous and organic phases will determine the predominant concentration of $^{11}$B in the organic phase due to the ratio $[\text{BO}_4^-] : [\text{BO}_3^-] = 1:2$ in the $y$- form extracted into the organic phase.

\[
\left[\text{^{10}BO}_3^-\right] + \left[\text{^{11}BO}_4^-\right] \leftrightarrow \left[\text{^{11}BO}_3^-\right] + \left[\text{^{10}BO}_4^-\right]
\] (10)

**Figure 2.** The conditional diagram of the distribution of components in a system with a secondary amine (organic phase above, lower aqueous)

4. Conclusions
As a result of phase and isotopic equilibrium studies in three extraction systems, an aqueous solution of boric acid – boric acid in the organic phase, where the organic phase is 0.5 M DEA in o-xylene (system 1), DPA (system 2), DBA (system 3), is established:
- the extraction coefficient $K_{\text{ex}}$ does not exceed the values that were previously obtained on a system with TBP;
- calculated the formation of various forms of boric acid at different pH values;
- based on the results of an isotopic analysis of equilibrium aqueous and organic phases, a single stage separation factor $\alpha$ is determined that is on the same level as the $\alpha$ for a system with TOA, but the concentration of the 10-boron isotope occurs in the aqueous phase, that is, inversion with respect to the previously considered systems, which due to the accumulation of four-coordinated boron in the aqueous phase during the partial dissolution of secondary amines in the aqueous phase;
- the mechanism of phase and isotopic distribution is proposed for systems where secondary amines are used as extractant.

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