Separation of boron isotopes by chemical exchange in liquid-liquid systems

A V Khoroshilov, P I Ivanov

Isotope Technology and Hydrogen Energy Department, Mendeleev University of Chemical Technology of Russian, 9 Miusskaya Square, Moscow 125047, Russian Federation

avkhor@inbox.ru

Abstract. The currently used technologies for the production of boron isotopes for nuclear power and nuclear medicine are based on the application of toxic boron halides. The report is devoted to alternative processes for enrichment of $^{10}$B and $^{11}$B by chemical exchange in extraction systems using boric acid, that is, without of boron halides. The results of studying phase and isotope equilibrium in two liquid-liquid systems are considered: an aqueous solution of boric acid – an organic phase in the form of tributyl phosphate or a solution of trioctylamine in o-xylene. The obtained values of the separation factor for boron isotopes characterize the predominantly phase isotope effect in the first system, and in the second system the effect of chemical isotope exchange. Accordingly, the values of the single stage separation factor are $1.0067 \pm 0.0035$ and $1.025 \pm 0.005$ and are close to similar values for rectification of boron trifluoride and chemical exchange in the anisole process of boron isotope separation. The practical use of the studied extraction systems may allow the separation of boron isotopes in the horizontal cascades of centrifugal extractors in the absence of an environmental hazard.

1. Introduction

Industrial separation of stable boron isotopes ($^{10}$B and $^{11}$B) is carried out by methods of low-temperature rectification of boron trifluoride BF$_3$ [1, 2], chemical exchange rectification in the system gaseous BF$_3$ – complex compound BF$_3$, for example, with dimethyl ether [3] and chemical isotope exchange in gas – liquid systems [4-6] (for example, BF$_3$ - BF$_3$·C$_6$H$_5$OCH$_3$). The described methods are based on the use of relatively expensive and dangerous compound – boron trifluoride BF$_3$ (relatively recently proposed new gas-liquid systems for boron isotope separation, unfortunately, are also based on the use of BF$_3$ [7-9].

As an alternative method of boron isotope separation can be considered the process of boric acid (H$_3$BO$_3$) extraction by organic liquid from aqueous solution. The first study of boron isotope separation by extraction was performed in the early 1960s in the system “aqueous solution H$_3$BO$_3$ – isoamyl alcohol” [10], 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-trihydrododecafluorohexanol and trioctylamine [11]: as the authors indicate, $\alpha$ was found to be not larger than 1.005.
It is possible that the use of other extractants can lead to the formation in the organic phase of boric acid complex, with the participation of which the isotope enrichment coefficient $\alpha = \varepsilon - 1$ will be greater.

The results of experimental studies of phase equilibrium and measurement of a single stage separation factor for boron isotopes in two extraction systems are considered in the article: system 1 - aqueous solution of boric acid - tributyl phosphate (TBP); system 2 - aqueous solution of boric acid – trioctylamine (TOA) in xylene.

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 ($\text{org}:\text{aq}$ or $\text{aq}:\text{org}$). Also in the experiments, the initial concentration of boric acid $C_\text{aq}$ was 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. The aqueous phase was investigated for determining the boron content and boron isotope composition, and the organic phase was re-extracted by distilled water.

Based on the results of quantitatively analysis and the equation of material balance, the extraction coefficient $K_D$ as the ratio of boron concentration $C_\text{org}^*$ in the equilibrium organic phase to the boron concentration $C_\text{aq}^*$ in the equilibrium aqueous phase was determined by equation (1):

$$K_D = \frac{C_\text{org}^*}{C_\text{aq}^*} \quad (1)$$

2.2. Isotope analysis

Isotope analysis of boron in boric acid both in initial and in equilibrated aqueous phase was carried out by ICP-MS method on the mass-spectrometer XSeries II (Thermo Scientific) relative to the isotope boron standard SRM 951 according to the previously developed method [12].

The influence of the total measurement time $I_t$ at a different values of the sweep frequency $S$ (from 100 to 3000) and the time of counting pulses $D_t$ (from 10 to 200 ms) was determined within the used method of isotope analysis. The choice of measurement optimal total time $I_t$ is illustrated in figure 1.

The sequence of measurements of the isotope ratio included the following steps: determination of the isotope ratio for the standard solution, flushing out by deionized water in the measurement mode, measurement of the boron isotope ratio in the sample under study, again flushing out by deionized water, re-determination of the isotope ratio to account the effect of mass discrimination

2.3. Quantitative analysis of boron in aqueous phase

Quantitative determination of boron in the aqueous phase ($C_\text{aq}$ and $C_\text{aq}^*$) was carried out using a scanning spectrometer Cintra 303 (GBC) and the test set “MET-B-PC” (MedEcoTest) similarly to method in [13].

It was determined the value of the maximum absorption $A$ observed at a wavelength 410 nm (figure 2). The calculation of boron concentration in the aqueous phase was made on a pre-established calibration dependence of absorption on the boron concentration (figure 3).
Figure 1. To the definition of the optimal total time of measurement $t_c$: $\Delta^{-11}B$; $\Delta^{-10}B$.

Figure 2. Maximum absorbance $A$ observed at 410 nm.

Figure 3. The calibration line for the determining of boron concentration $C$ (values of absorbance at 410 nm).

3. Results and discussion

3.1. Phase equilibrium

As a result of the study of phase equilibrium in liquid – liquid systems, where TBP (system 1) and TOA (system 2) were used as an organic phase, dependences of extraction coefficients on the initial concentration of boric acid (boron) in the aqueous phase (figure 4 and 5) were obtained.

For system 1, there is a weak increase in the values of extraction coefficients from the initial concentration of boric acid in the aqueous phase, and this trend is observed regardless of the ratio of the volume of phases throughout the studied boric acid concentration range. And yet the value of the extraction coefficient is very small and does not exceed 0.2 and the dependence of the extraction coefficient on the initial concentration of boric acid in the aqueous phase for system 1 described by equation (2):

$$K_D = 3.18 \times 10^{-2} \times \ln(C_{aq}^{+}) + 0.214 \quad (2)$$
Figure 4. The concentration of boric acid at equilibrium in organic and aqueous phases and extraction ratio for system 1 (single dependencies for different volumetric phase ratios org:aq: 1:1; 2:1; 3:1).

Figure 5. The change in the extraction coefficient as a function of initial concentration of boric acid in aqueous phase for system 2.

The small values of the extraction coefficient for system 1 can be explained by the lack of formation of a sufficiently stable boric acid – TBP complex under these experimental conditions, which may imply a boric acid extraction mechanism based on partial mutual dissolution of phases in each other.

For system 2, there is a characteristic change in the values of the extraction coefficient for extraction processes, which manifest itself in a decrease in the extraction coefficient with an increase in the initial boron concentration in the aqueous phase. It should be noted that the presence of tartaric
acid in the system 2 is due to the fact that in the absence of tartaric acid, there was no observed transition of boron into the organic phase, which can be explained by the presence of a steric effects between TOA and boric acid. The dependence of the boric acid extraction coefficient on the initial boron concentration in the aqueous phase for system 2 is described by equation (3):

\[ K_D = 2.322 \times \left(C_{aq}^{+}\right)^2 - 34.743 \times C_{aq}^{+} + 131.36 \]  

(3)

3.2. Flow reflux: re-extraction of boric acid

For the considered liquid – liquid systems, re-extraction of boric acid with distilled water was considered as a method of flow reflux of boron from the organic phase to the aqueous phase. As a parameter characterizing the re-extraction efficiency, the re-extraction degree was used, which was calculated according to equation (4):

\[ \Gamma_{\text{Re-ex}}, \% = \frac{n_{aq}^*}{n_{org} + n_{org}^*} \times 100 = \left(1 + \frac{K_D \times V_{org}}{V_{aq}}\right)^{-1} \times 100 \]  

(4)

The figures 6 and 7 show that the increase in the volume of re-extractant, that is distilled water, during re-extraction leads to a characteristic increase in the re-extraction degree.

Figure 6. Boric acid re-extraction degree \( \Gamma_{\text{Re-ex}} \), depending on the volume ratio of re-extractant (aq) to the organic phase (org) for system 1 at room temperature: ● – multiplicity of re-extraction; ○ – single re-extraction by increasing the volume of re-extractant

For example, the system 1 is shown (figure 6) that the increase of multiplicity of re-extraction with equal volumes of the phases leads to the achievement of higher values of the degree of re-extraction with a lower total use of distilled water than the volume increase re-extractant in a single-step balances. At the same time, relatively high values of the degree of re-extraction are observed for system 1 already at room temperature.
Figure 7. Boric acid re-extraction degree $\Gamma_{\text{Re-ex}}$, depending on the volume ratio of re-extractant (aq) to the organic phase (org) for system 2: ○ – room temperature; ■ – 75.5 °C.

For system 2, the increase on the re-extractant volume, as for system 1, leads to an increase in the degree of re-extraction. However, a relatively significant transfer of boron from the organic phase to the aqueous phase is observed only with an increase in temperature, which, like the data in the figure 7, may indicate the formation in the organic phase of sufficiently strong complexes of boric acid – tartaric acid – TOA.

3.3. The values of the single isotope effect and its comparison with the separation factors of the industrial methods of boron isotopes separation

To determine the value of a single isotope effect in systems 1 and 2, the values of the isotope ratio $R$ of the initial aqueous phase and the aqueous phase after equilibration with the organic phase were determined. Isotope ratio $R$ is the ratio of isotope concentrations of boron-11 to boron-10, which looks like equation (5):

$$R = \frac{11\ B}{10\ B}$$

In this case, taking into account the isotope ratio for SRM 951 ($R^\text{st}$), the true value of the isotope ratio, for example for the equilibrium aqueous phase, is determined by equation (6):

$$R^*_{\text{true}} = R^*_{\text{measured}} \times \left( \frac{R^\text{st}_{\text{true}}}{R^\text{st}_{\text{measured}}} \right)$$

According to the results of the isotope ratio measurements, it was found that during the extraction of boric acid the $^{10}$B is concentrated in the organic phase, and the isotope $^{11}$B, respectively, in the aqueous phase. In accordance with the equation of material balance, the value of a single stage isotope effect was determined by equation (7):

$$\alpha = \frac{R^*_{\text{true}}}{R^*_{\text{true}}}$$

Table 1 presents a comparison of the single stage separation factors of boron isotopes for the methods of boron trifluoride rectification, chemical exchange rectification and chemical isotope
exchange in the system with anisol, and $\alpha$ values in the investigated extraction systems: system 1 and system 2.

Table 1. The single stage separation factors for gas – liquid (industrial technology) and liquid – liquid (R&D technology) systems.

| Industrial technology | System     | $T$, K | Single stage isotope effect $\alpha$ |
|-----------------------|------------|--------|-------------------------------------|
| Low-temperature rectification BF$_3$ | 170        | 1.0085 |
| Chemical exchange rectification BF$_3$ – CH$_3$OCH$_3$BF$_3$ | $\approx$400 | 1.015  |
| Chemical isotope exchange BF$_3$ – C$_6$H$_5$OCH$_3$BF$_3$ | 293        | 1.0300 |
|                                           | 338        | 1.0260 |

| R&D technology | System 1 | $T$, K | Single stage isotope effect $\alpha$ |
|----------------|----------|--------|-------------------------------------|
| Extraction in the liquid – liquid system | 293-295  | $1.0067 \pm 0.0035$ |
| System 2      | 1.0250 $\pm 0.0050$ |

The measured value of the single stage separation factor of boron isotopes in system 1 is equal to $1.0067 \pm 0.0035$ and is comparable with the same value for low-temperature rectification of boron trifluoride, and the value of $\alpha = 1.0250 \pm 0.0050$ in system 2 corresponds to the isotope effect of chemical exchange between BF$_3$ and its complex with methyl phenyl ether or anisole. On the basis of the measured alpha values, it can be assumed that in the first system the isotope effect corresponds to phase isotope exchange, but in the second, to predominantly chemical isotope exchange.

4. Conclusions
As a result of phase and isotope equilibrium studies in two extraction systems, an aqueous solution of boric acid – boric acid in the organic phase, where the organic phase is tributyl phosphate (system 1) or trioctylamine in o-xylene (system 2), is established:

- at room temperature, the extraction factor in system 1 is much less than unity, equal to 0.2 and practically independent of the concentration of boric acid in water;
- in system 2, the extraction factor is significantly higher (as a minimum by an order of magnitude) and sharply changes with a change of boric acid concentration in the aqueous phase, increasing as it decreases;
- the lighter boron isotope (boron-10) in the studied systems is concentrated in the organic phase;
- the measured value of the single stage separation factor of boron isotopes in system 1 is equal to $1.0067 \pm 0.0035$ and is comparable with the same value for low-temperature rectification of boron trifluoride;
- the value of a single boron isotope separation factor in system 2 was $1.0250 \pm 0.0050$, which corresponds to the isotope effect of chemical exchange between boron trifluoride and its complex with methyl phenyl ether or anisole;
- the isotope effect in system 1 corresponds to the phase isotope effect, and in system 2 – to the effect of chemical isotope exchange;
- from the flow reflux point of view, in order to achieve the required concentration of boron-10 isotope, either multistage or cross re-extraction of boric acid from the organic phase is necessary.

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