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# Recovery of Boric Acid from Aqueous Solutions Using Polycondensation Anion Exchangers

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**Abstract.** The sorption behavior and mechanism of boric acid recovery on polymerization anion exchangers of both strongly and weakly basic types are now fairly well understood, while a current knowledge of the sorption of boric acid on polycondensation anion exchangers is limited. The present investigation was carried out to establish influences of temperature, concentration and pH of boric acid on its sorption behavior. It was used polycondensation anion exchangers based on monoethanolamine and epichlorohydrin (SB-1, SB-2) and pyrocatechol and formaldehyde (SB-7, SB-8). It has been revealed that anion exchangers in the hydroxyl form containing alcohol and aminooxyethyl functional groups possess high sorption activity and selectivity for boron. When sorption of boric acid from solutions at a concentration more than 0.057 M, pH 5.0-7.5, the exchangers have been shown to possess unusually high sorption capacity for boron. It has been established that the mechanism of boric acid sorption on the hydroxyl-form polycondensation anion exchanger has the mixed nature owing to the fact that it was observed two simultaneous processes: first, chemisorption of boric acid molecules by the hydroxyl groups of the anion exchangers, coupled with the accumulation of tetraborate anions  $[B_4O_5(OH)_4]^{2-}$  in the sorbent phase, and second, complex formation of polynuclear boron compounds.

## 1. Introduction

Boron and its compounds are widely used in various sectors of the economy. They are used in the manufacture of ceramic products, various alloys, glass, protective coatings, refractory materials, heat-resistant fibers, as well as a dry lubricant in bearings. Boric acid is used as a neutron absorber in a Pressurised Water Reactor (PWR) in nuclear power plants. Increase in demand for boric acid in Russia stimulates developing effective technology and technical solutions for the recovery of boron from natural and industrial wastewaters, as well as from spent technological solutions after the production of boric acid and its salts [1]. The analysis of modern technologies and the best of available applications [2] revealed the sorption is the best solution for the recovery of boron from aqueous solutions.

The sorption behavior of boron on sorbents of both inorganic and organic nature is described in the literature [3-5]. Double metal hydroxide-based sorbents possessed a hydrocalcite structure, for example, *magnesium-aluminum* hydroxide and magnesium-iron hydroxide, exhibit high selectivity for boron. The maximum value of the capacity of these sorbents (75 mg/g) is observed in the pH range 7.5–8.5, at which boron is in the solution as anions,  $[B_4O_5(OH)_4]^{2-}$  [3]. When extracting boron with organic sorbents, for example, strong base polymerization anion exchangers, it was found that their



sorption capacity with respect to boron anions depends on the ion exchanger nature, its functional groups, as well as the initial salt form of the ion exchanger and the solution acidity [4, 5]. Monofunctional strong base anion exchangers of type AB-17 in the OH-form exhibit the maximum sorption of boron from solutions in the pH range 10.5–11.0, which is typical for sorption of boron in the form of trihydroxoborate anions,  $B_3(O_3OH)_5^{2-}$  [5]. At the same time, there is lack of knowledge on the boron behavior on polycondensation anion exchangers, despite the fact that in the second half of the twentieth century, boron selective polycondensation anion exchangers were synthesized in Russia.

This paper presents the results of a study of the influence of various salt forms of boron selective anion exchangers, as well as temperature, acidity of the medium, and concentration of boric acid on its recovery from aqueous solution.

## 2. Objects and research methods

The objects of the study are boron selective polycondensation anion exchangers of the SB type. Anion exchangers SB-1 and SB-2 are synthesized on the base of monoethanolamine and epichlorohydrin containing aminoxyethyl functional groups. These ion exchangers differ from each other in the nature of the hardener: diaminoisopropanol was used as hardener for synthesizing SB-1 anion exchanger, and glycerol monochlorohydrin was used for SB-2. The initial products for synthesizing both SB-7 and SB-8 anion exchangers were pyrocatechol and formaldehyde, this fact results to the presence of functional phenolic hydroxyl and alcohol groups in their structure and the absence of amino-containing ones.

Both preparation of anion exchangers and determination of the static exchange capacity (SEC) of the examined anion exchangers with HCl were carried out according to GOST 10896-64 regulations (Russian Federation). Anion exchangers were activated by conversion to the Cl-, OH- and SO<sub>4</sub>-forms with 1N solutions of HCl, NaOH, and H<sub>2</sub>SO<sub>4</sub>, respectively. The sorption properties of anion exchangers with respect to boron ions in aqueous solutions of boric acid were studied under static conditions.

Techniques for studying sorption equilibrium at various pH, sorbate concentrations, and temperatures were used to establish the effect of a chemical structure of the sorbents on their ability to interact with boron ions. Samples of the previously prepared anion exchangers (0.25 g) were placed in 100 ml round flat-bottomed flasks, added 50 ml of boric acid solution at various concentrations, then placed inside a thermostated cell, and changing solution temperatures, had been testing on a laboratory shaking table for 24 hours. The concentration of boric acid was varied in the range of 0.05–0.5 M, pH of the solutions was varied within 1–11, and the temperature was 20–80 °C.

The amounts of boron extracted from solutions were calculated from the difference between its concentrations in the initial and equilibrium solutions, determined by titration of the sample with 0.1N NaOH solution containing phenolphthalein in the presence of mannitol (hexatomic alcohol - aldite C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>) according to GOST 18704-78 regulations (Russian Federation). To study the kinetics of boron sorption was used the individual sample weight method [6], and the kinetic parameters of the sorption were calculated according to practical standards [7].

To establish the mechanism of boron sorption by ion exchangers, the infrared spectroscopy method was used. Infrared spectra of the studied samples were recorded on a Nicolet 380 IR Fourier spectrometer in the wavelength range 700–4000 cm<sup>-1</sup>. The samples were prepared as KBr tablets.

## 3. Results and discussion

Analysis of the published works in the field has showed that interpretation of the experimental data of the sorption extraction of boron and its compounds from aqueous solutions is sometimes confusing and difficult to understand. This is due to the fact that in aqueous solutions boron is in the form of simple and polyanions, the composition of which depends on the boric acid concentration and the solution acidity. It is known that boric acid does not act as a proton donor, but as a Lewis acid, which is characterized by the addition of water hydroxyl ions with the formation of hydroxoborate anion,

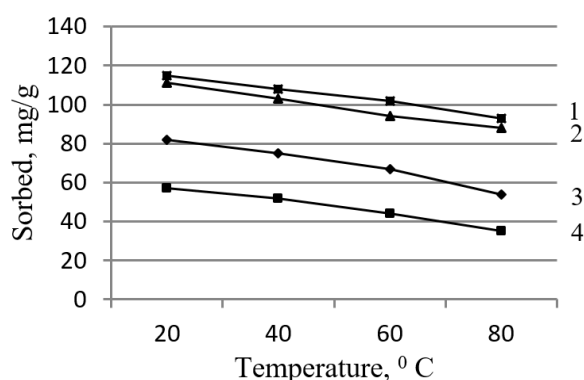
$[B(OH)_4]^-$ . In dilute aqueous solutions of boric acid, a hydroxoborate anion is capable of exchanging with the OH groups of the anion exchanger.

Changing an aqueous solution acidity and a boric acid concentration leads to the formation of polymeric forms of boric acid – tri- and tetraborate anions,  $[B_3O_3(OH)_4]^-$  and  $[B_4O_5(OH)_4]^{2-}$  [3]. Thus, the possibility of the simultaneous presence of different forms of boron- oxygen compounds at the definite pH and concentration of boric acid in the aqueous solution must be taken into account when studying its sorption behavior on anion exchangers. In discussing the results of the study, we will adhere to generally accepted ideas about the content of various forms of boric acid anions in aqueous solutions.

Preliminary studies have established the influence of the ionic form of anion exchangers and temperature on their sorption activities for the recovery of boron from 0.057 M boric acid solution at a temperature of 20 °C. The pH of the solution was in the range of 4.5–4.8 (Table 1, Figure 1).

**Table 1.** Values of sorption of boron by various ionic forms of anion exchangers.

Type	Sorption values					
	OH-form		Cl-form		SO <sub>4</sub> <sup>2-</sup> – form	
	mg/g	mmol/g	mg/g	mmol/g	mg/g	mmol/g
SB-1	118.1	1.90	14.0	0.23	21.9	0.35
SB-2	114.3	1.84	14.2	0.23	20.9	0.34
SB-7	54.9	0.88	16.2	0.26	16.3	0.26
SB-8	39.4	0.64	9.3	0.15	15.9	0.25

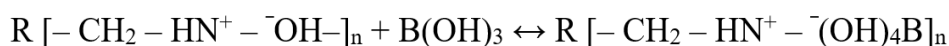


**Figure 1.** Relationship between temperature and sorption of boric acid with OH form of anion exchangers: 1 – SB-1; 2 – SB-2; 3 – SB-7; 4 – SB-8 ( $C_{H_3BO_3} = 0.057$  M; pH = 4.5).

The maximum sorption activity and selectivity with respect to boron from aqueous  $H_3BO_3$  solutions are performed by the studied anion exchangers in hydroxyl form. In salt forms formed by anions of stronger mineral acids than boric one, anion exchangers perform low sorption values of boron, which is in good agreement with experimental data published in [8]. Among the sorbent types possessing different chemical nature of their polymer matrixes and functional groups, anion exchangers of SB-1 and SB-2 deserve special attention. The sorption values of boric acid on these sorbents are 2–3 times higher than on SB-7 and SB-8 anion exchangers. In our opinion, there are two reasons to explain the phenomenon.

First, the static exchange capacity of the anion exchangers synthesized on the base of monoethanolamine and epichlorohydrin (SB-1 = 7.62 mg·equiv/g, SB-2 = 6.88 mg·equiv/g) is 3 times higher than the similar characteristics of anion exchangers SB-7 and SB-8 (2.66 mg·equiv/g and 1.91 mg·equiv/g, respectively). Second, boric acid extraction from the solution is stimulated with the presence of aminoxyethyl functional groups, for which the degree of ionization increases in acidic solutions, in the structure of SB-1 and SB-2 anion exchangers.

Despite the difference in the sorption values, it can be assumed that sorption extraction of boric acid from weak acid diluted aqueous solutions has the same mechanism for all the examined anion exchangers. Considering anion exchangers in hydroxyl form as analogues of a concentrated alkaline solution, then the extracting boric acid from the solution at the initial stage of sorption should be carried out by the chemisorption mechanism. The priority existence of forms of undissociated boric acid in dilute solutions in the absence of strong acids [9] suggests that the interaction between boric acid molecules and hydroxyl functional groups of anion exchange resin leads to the formation of fairly stable hydroxoborate forms  $[B(OH)_4]^-$ :

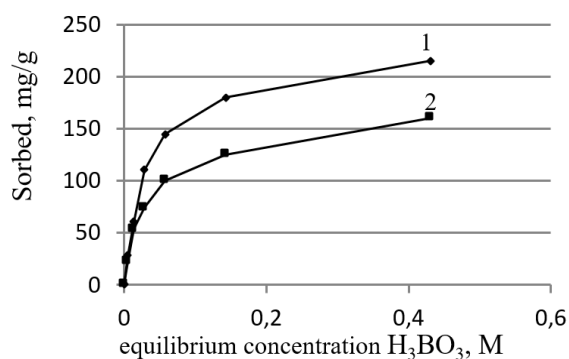


This is confirmed with experimental data. Thus, it was found that in the initial period of sorption, when the degree of saturation of anion exchangers with boron does not exceed 50–55% of the ion-exchange capacity value, first, the absorption bands are at about  $920\text{ cm}^{-1}$  in the infrared spectra of the samples, which corresponds to the stretching vibrations of B-O bond in the oxygen-containing boron compounds containing boron with the coordination number of 4, and second, the absence of absorption bands at  $1350\text{ cm}^{-1}$ , which is typical for polyborate forms of boric acid [5].

As the anion exchanger is being saturated, the concentration of free functional hydroxyl groups is becoming low, and the concentration of  $[B(OH)_4]^-$  ions is comparable with their *ion*-exchange capacity value, polymer forms of boric acid are forming in the anion phase by sorption of boric acid molecules onto free tetrahydroxoborates anions, which is confirmed by the presence of absorption bands in the IR spectra of the saturated anion exchanger samples in the  $1350\text{--}1420\text{ cm}^{-1}$  region, which is typical for the polymeric forms of boric acid,  $[B_4O_5(OH)_4]^{2-}$  [4]. In this case, the SB-1 and SB-2 anion exchangers, containing aminoxyethyl functional groups, show the most boron affinity.

The experimental fact of a decrease in the sorption value of boric acid with an increase in the temperature of the solutions directly confirms the formation of polymer forms of boric acid inside the anion exchangers by the mechanism under consideration (Figure 1). It is known [10] that the total proportion of polyborate forms of boric acid decreases with an increase in solution temperature due to their low thermal stability, which contributes to the process of their dissociation into mononuclear particles.

It has been established that in the initial period, boric acid is extracted with the OH form of the anion exchangers from dilute solutions by chemisorption on free functional groups with the formation of hydroxoborate anions,  $[B(OH)_4]^-$ . The isotherms of boron sorption by the SB-1 and SB-2 anion exchangers, obtained under static conditions at a temperature of  $20 \pm 2\text{ }^\circ\text{C}$ , are convex in nature without saturation, and are more satisfactorily described by the Freundlich equation (Figure 2).



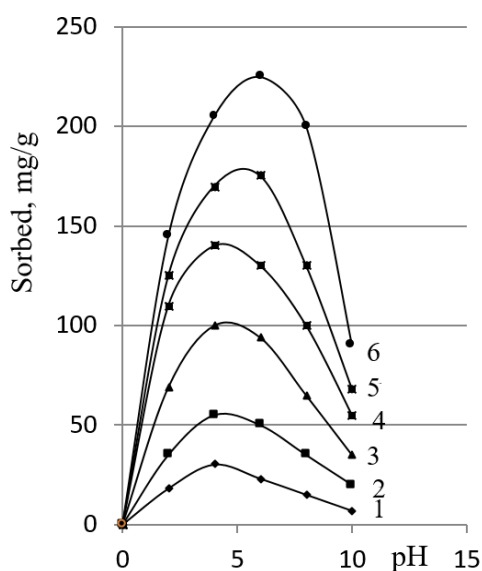
**Figure 2.** Sorption isotherms of boron by SB-1 (1) and SB-2 (2) anion exchangers from boric acid solution at temperature  $20\text{ }^\circ\text{C}$ .

The silica gel modified with a formazan is characterized by the absorption band around  $420\text{ nm}$  which corresponds to a maximum absorption of partially polar formazan in the solution (Figure 3).

The steep initial portion of the sorption isotherms at an equilibrium concentration of boric acid in the range of 0.01–0.1 M characterizes a high degree of interaction between the sorbent and the sorbate. Analysis of the sorption isotherms shows that when an equilibrium concentration of boric acid is 0.1 M, the sorption extraction of boron by these anion exchangers is 75 wt. % of their maximum sorption from a highly concentrated solution (0.43 M). This is also confirmed by the values of sorption affinity values equal to 11.0 and 9.8 L mmol<sup>-1</sup>, calculated respectively for sorbents SB-1 and SB-2. This type of isotherm is characteristic for the sorption of ions having large radii and located close to each other, provided that there is a strong interaction between them.

Studies of the effect of solution acidity and boron concentration on its sorption behavior, as well as the kinetic characteristics of the sorption, were carried out on the SB-1 anion exchanger as the most effective sorbent.

The experimental results of the influence of solution acidity and boric acid concentration on the sorption behavior of the anion exchanger confirm the absence of the process of equilibrium saturation of the sorbent with oxygen-containing boron compounds in the entire range of the studied pH values. The sorption extraction curves for different acidities of the solution have the pronounced extremum, which shifts toward higher pH values of the solution and it is in the range pH 4.0–7.5, while increasing the initial concentration of boric acid (Figure 3).



**Figure 3.** Relationship between pH and boron sorption by SB-1 anion exchanger from boric acid solutions at different concentrations, M: 1 – 0.005; 2 – 0.014; 3 – 0.029; 4 – 0.057; 5 – 0.145; 6 – 0.43.

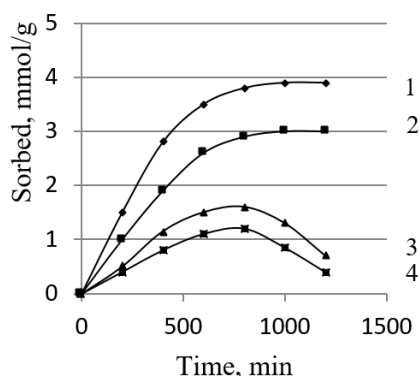
When the concentration of boron in the solution is up to 0.029 M, the maximum extraction of boron is observed in the range of pH = 4.5–5.0. An increase in the concentration of boron in the solution up to 0.43 M shifts the absorption maximum to pH = 6.0–8.0, which indicates there are different forms of borate ions sorbed by the anion exchanger. Such relationship between the sorption behavior of the anion exchanger and increases in both the concentration of boric acid and pH of the solution confirms the previously expressed hypothesis about the sorption mechanism of boric acid from diluted solutions.

As the concentration of  $[B(OH)_4]^-$  anions in the resin phase increases, sorption of boric acid occurs on free mononuclear borate anions with the formation of boron polynuclear complexes of the composition  $[B_4O_5(OH)_4]^{2-}$ , which are unstable in alkaline media decaying to mononuclear particles. This fact explains the sharp decrease in sorption of boric acid and the appearance of an extremum in the experimental sorption curves.

Attention is also drawn to such an experimental fact as occurring so called “super-equivalent” sorption of boric acid from its solutions at a concentration more than 0.057 M, pH 5.0–7.5 (Figure 3, lines 5 and 6). So, when *ion-exchange* capacity value of SB-1 anion exchanger is equal to 7.62

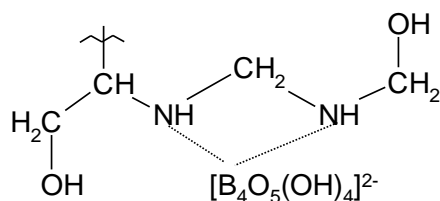
mg·equiv/g, sorption of boric acid from 0.145 M solution is 8.47 mg·equiv/g, and from 0.43 M solution it is 10.64 mg·equiv/g.

Based on the obtained experimental data, it can be concluded that the sorption of boric acid on the SB-1 anion exchanger is carried out by two complementary mechanisms. First, sorption extraction occurs owing to chemisorption of boric acid by the hydroxyl groups of the anion exchangers coupled with the accumulation  $[B_4O_5(OH)_4]^{2-}$  anions in the sorbent phase, and second, complex formation of boron compounds when a donor-acceptor bond between aminoxyethyl functional groups and a nitrogen atom forms. The presence in the infrared spectra of the SB-1 anion exchanger samples saturated with boron, intense absorption bands in the range of 1530–1500  $cm^{-1}$ , typical for the stretching vibrations of B-O bond, at the same time, their absence in the boron-containing sample of the SB-7 anion exchanger, confirms the involving of nitrogen in functional groups in coordination with the boron atom. The results of kinetic studies also confirm the presence of a mixed mechanism of boron sorption on anion exchangers (Figure 4).



**Figure 4.** Kinetics of boron acid sorption on SB-1 anion exchanger at different temperatures,  $^{\circ}C$ : 1 – 20; 2 – 40; 3 – 60; 4 – 80 (concentration  $H_3BO_3$  0.43 M; pH = 4.8).

Thus, high values of the rate constant of boron sorption at 20 $^{\circ}C$  ( $0.22 \cdot 10^2, s^{-1}$ ) and diffusion coefficient ( $D = 7.32 \cdot 10^6, cm^2/s$ ) calculated for the kinetic curve of boron sorption for 500 min at 20 $^{\circ}C$ , are typical both for the formation of mononuclear forms of boron and the external diffusion mechanism of boric acid sorption by the SB-1 anion exchanger. A further decrease in the intensification of boron sorption is explained with the formation of complex compounds and coordination bond between boron and the nitrogen atom in aminoxyethyl functional groups (Figure 5). In this case, each functional group has 2 boron atoms, which determines so called «super-equivalent» boron content in the anion exchanger.



**Figure 5.** Scheme of the formation of a complex compound of boron inside the anion exchangers.

#### 4. Conclusion

Thus, the hydroxyl-form polycondensation anion exchangers exhibit a higher sorption ability and selectivity while extracting boric acid, both from diluted and concentrated aqueous solutions, in comparison with salt forms formed by anions of stronger mineral acids than boric one. It was found that the extraction of boric acid by the SB-1 anion exchanger based on monoethanolamine and epichlorohydrin occurs owing to chemisorption of boric acid by the hydroxyl groups of the anion

exchangers coupled with the accumulation of tetraborate anions,  $[B_4O_5(OH)_4]^{2-}$ , in the sorbent phase, and second, complex formation of polynuclear boron compounds at the nitrogen atom of aminoxyethyl groups. The presence of «superequivalent» boron sorption established for the SB -1 anion exchanger determines its potential for utilization of boric acid and its compounds from industrial wastewater and waste technological solutions.

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