Creating an effective wood protectors from boric acid and aminoalcohols

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Abstract. The study of the composition and structure of the reaction products formed in the systems: boric acid – monoethanolamine – water and boric acid – diethanolamine – water at an equimolar ratio of acid and alcohol in an alkaline environment. Using IR-spectroscopy, \(^1\)H and \(^11\)B NMR-spectroscopy revealed the formation of monoethanolamine(N→B)-threehydroxyborate and diethanolamine(N→B)-threehydroxyborate, in which the nitrogen and boron atoms are coordinated. In the process of drying the resulting product due to intramolecular condensation, a cyclic structure is formed. In the composition of the boron-nitrogen compounds obtained, the boron atom has a coordination number of four. The resulting boron-nitrogen compounds are effective antiseptics of wood building structures, and also exhibit flame retardant properties. There is boron-nitrogen coordination in the composition of the modifier molecule, due to which nucleophilic attack by water molecules is excluded. Therefore, the modifier is firmly fixed in the composition of the wood and provides durable protection against bio-corrosion and fire.

1. Introduction

The interaction of boric acid with aminoalcohols is of great practical importance, since the resulting products are used as corrosion inhibitors for metals [1], and antiseptic and flame retardants for wood [2]. By now, however, there is no consensus on the composition and structure of the products obtained during the interaction. The systems of boric acid – monoethanolamine – water pH 10.9 and boric acid – diethanolamine – water, formed with a threefold molar excess of boric acid at pH 6, were studied by the isothermal solubility method, refractometry, and IR-spectroscopy in [3, 4]. The authors stated that ammonium salts of the following compositions are formed: monoethanolammonium triborate \([\text{HO(CH}_2\text{H}_2\text{N}_2\text{H}_3}]^+(\text{H}_4\text{B}_3\text{O}_7)^{-2}\text{H}_2\text{O}\) and diethanolammonium triborate \([\text{(HOC}_2\text{H}_4\text{H}_2\text{N}_2}]^+(\text{H}_4\text{B}_3\text{O}_7)^{-2}\text{H}_2\text{O}\) with cyclic structure of the trimetaborate anion.

Our aim was to study the composition and structure of the reaction products formed in the systems of boric acid – monoethanolamine – water pH 10.9 and boric acid – diethanolamine – water pH 10.2. Under standard conditions, at an equimolar ratio of acid and alcohol, the formation of polyborates is excluded [5]. The characteristic and dominant type of bond between the B and N atoms in the ligand system is the coordination bond due to the tendency of the boron atom to compensate for the electron deficit, and the presence of the lone electron pair in nitrogen of an amino alcohol. The boron-nitrogen bond is formed via the donor-acceptor mechanism, which results in a change of the boron and nitrogen coordination numbers from 3 to 4 and stabilization of the compounds obtained.
2. Methodology
The interaction products in the systems of boric acid – monoethanolamine – water and boric acid –
diethanolamine – water were investigated by means of FTIR spectroscopy, $^1$H and $^{11}$B NMR
spectroscopy and quantitative organic elemental analysis. Boron was quantified
spectrophotometrically as a complex with azomethine-H [6]. Nitrogen, carbon and hydrogen were
quantified using Carlo Erba 1106 automatic elemental analyzer.

The IR absorption spectra of boric acid, mono- and diethanolamine, as well as the product of their
interaction were recorded by Magna-750 FTIR spectrometer (Nicolet, USA) with a spectral resolution
of 2 cm$^{-1}$. Boric acid was ground with KBr (approximately 1:50 by mass), pressed into disks that were
used to record spectra. The spectra of mono-, diethanolamine, and reaction products were obtained
from thin liquid films between the potassium bromide windows.

$^1$H and $^{11}$B spectra were recorded on the Bruker Avance 400 spectrometer with operating frequencies
400.13 MHz and 128.38 MHz, respectively, using tetramethylsilane Si(CH$_3$)$_4$ and boron trifluoride
diethyl etherate BF$_3$-OEt$_2$, respectively, as external standards.

3. Result and discussion
The IR spectra of boric acid, mono- and diethanolamine and the products of their interaction after
drying are presented in Figure 1 and 2. In the IR spectrum of monoethanolamine, the absorption band
with a frequency of 1597 cm$^{-1}$, corresponds to the asymmetric planar deformation vibrations of the –
NH$_2$ group (Figure 1b). In the spectrum of the resulting product, this absorption band shifts to the low-
frequency region (Figure 1c), which is caused by the boron-nitrogen bond formation [7, 8]. As it is
known from the literature [9], the absorption band in the region of 1200 cm$^{-1}$ results from the
stretching vibration of the N $\rightarrow$ B bond in the tetrahedron, the peaks of this frequency are present in
the spectra of the interaction products of boric acid with mono- and diethanolamine.
Figure 1. IR-spectra of boric acid (BA) – a, monoethanolamine (MEA) – b, interaction product of BA and MEA – c.

Figure 2. IR-spectra of boric acid (BA) – a, diethanolamine (DEA) – b, interaction products of BA and DEA – c.

The band of deformation vibrations of the NH-group (1656 cm\(^{-1}\)) in the IR spectrum of diethanolamine is weakly expressed in Figure 2b. As compared to the absorption band of free diethanolamine, the shift of this band in the spectrum for the interaction products of boric acid with diethanolamine (Figure 2c) to the low-frequency region is due to a change in the coordination number of the nitrogen atom [7, 8], caused by the boron-nitrogen bond formation.
The $^{11}$B NMR spectra of aqueous solutions of the reaction products of boric acid with mono- and diethanolamine are presented in Figure 3. According to [5], the effect of solvents on $^{11}$B chemical shifts in the NMR spectrum is negligible, except for the case when the reaction proceeds between the boron-containing compound and the solvent. The $^{11}$B chemical shift for a boron-containing compound can therefore be considered as a characteristic constant for identification purposes. To identify the products of the boric acid interaction with amino alcohols, the interaction products were dissolved in D$_2$O and the $^{11}$B NMR spectra were recorded on the Bruker Avance 400 spectrometer.

![Figure 3. $^{11}$B NMR spectra of aqueous solutions of the interaction products of boric acid and monoethanolamine – a, boric acid and diethanolamine – b.](image)

In the $^{11}$B spectrum of the interaction product of boric acid with monoethanolamine (Figure 3a), a shift of 5.5 ppm is observed, which, according to [10], corresponds to the structure of monoethanolamine(N→B) trihydroxyborate (1), where nitrogen and boron are coordinated:

$$\text{(OH)}_3\text{B} \leftrightarrow \text{NH}_3(\text{CH}_2)\text{OH}$$

(1)

Two shifts are easily notable in the spectrum of Figure 3b. The first shift 9.2 ppm corresponds to the structure of diethylamineborate (2), which can be represented by the formula [9]:

![Diagram](image)

$$\text{H} \cdots \text{B} \cdots \text{N} \cdots \text{H}$$

(2)

The second shift 5.8 ppm corresponds to the structure of diethanolamine (N→B) trihydroxyborate [10]:

$$\text{(OH)}_3\text{B} \leftrightarrow \text{NH}(\text{CH}_2\text{OH})_2$$

(3)

The mass ratio (2) to (3) is 3:1 in accordance with the intensity of the peaks.

It is important to note, there is no chemical shift of 20 ppm in $^{11}$B spectra (Figure 3), which is characteristic to the boron atom in the composition of boric acid. This fact reflects full interaction of boric acid with amino alcohols under the given experimental conditions.
As it was established by comparison of the $^{11}$B NMR spectra of the reaction products in an aqueous medium and after drying (Figure 3, 4), cyclic structures (a) and (b) are formed in the process of intramolecular condensation during drying [10]. The signal in the region of 10.7 ppm of the $^{11}$B NMR spectrum of the interaction products of boric acid and diethanolamine corresponds to the diethylamine(N→B)borate tautomer – diethylaminoborate (c) [10], the mass ratio of tautomers is 1:1 (Figure 4).

![Figure 4](image-url)

**Figure 4.** $^{11}$B NMR spectra of the interaction products of boric acid and monoethanolamine – a, boric acid and diethanolamine after drying - b.

![Cyclic structures](image-url)

**Figure 5.** Cyclic structures.

It was proved by the $^1$H NMR spectroscopy (Bruker Avance 400) using dimethyl sulfoxide as a solvent that the interaction products of boric acid with amino alcohols did not contain ammonium salts. In the $^1$H NMR spectra of the dried interaction products (Figure 5), a number of signals characterizing the proton resonance of the solvent (dimethyl sulfoxide) at 2.5 ppm, amino groups at 2.6 ppm, methylene groups at 3.4 and 3.6 ppm, acid hydroxyls at 4.0 ppm were identified [11]. While a 3.0 ppm shift characteristic to protons of ammonium groups, is absent in $^1$H NMR spectra of the studied products (Figure 6).
Figure 6. $^1$H NMR-spectra of the interaction products of boric acid and monoethanolamine – a, boric acid and diethanolamine after drying - b.

The experimental data are in correlation with the theoretically calculated mass content of elements, expressed as a percentage, which confirms the assumed structure of the interaction products of boric acid with mono- and diethanolamines.

Thus, in this work, it was established for the first time that the product of interaction of equimolar amounts of boric acid and monoethanolamine in the aqueous medium is monoethanolamine (N→B) trihydroxyborate, which, when dried, turns into monoethylamine(N→B)-borate. Interaction of equimolar amounts of boric acid and diethanolamine in an aqueous medium results in formation of diethylaminoborate and diethanolamine(N→B)-trihydroxyborate in a 3:1 ratio by weight. And upon drying the interaction mixture, tautomers are formed: diethylamine(N→B)borate and diethylaminoborate in a ratio of 1:1 by weight. The resulting boron-nitrogen compounds are effective antiseptics of wood building structures [12-16], and also exhibit flame retardant properties [17-20]. This is due to boron-nitrogen coordination in the composition of the modifier molecule, due to which nucleophilic attack by water molecules is excluded. And therefore, the modifier is firmly fixed in the composition of the wood and provides durable protection against bio-corrosion and fire.

References

[1] Alekperov E, Reznik A 2000 Boron complexes: synthesis, application (Moscow: MSU)
[2] Koteneva I, Kotljarova I, Sidorov V 2010 Stroitelnyye materialy 6 pp 56-60
[3] Skvortsov V, Molodkin A, Petrova O, Tsekhanskaya N, Rodionov N 1980 Russian Journal of Inorganic Chemistry 1 25 pp 1964-1969
[4] Skvortsov V, Molodkin A, Rodionov N, Tsekhanskaya N 1981 Russian Journal of Inorganic Chemistry 5 26 pp 1389-1393
[5] Niedenzu K, Dawson J 1968 Chemistry of boron-nitrogen compounds (Moscow: Mir)
[6] Gelman N, Terentyeva E, Shanina T 1987 Methods of quantitative organic elemental microanalysis (Moscow: Khimia)
[7] Nakamoto K 1991 Infrared and Raman spectra of inorganic and coordination compounds (Moscow: Mir)
[8] Smith A 1982 Applied IR Spectroscopy (Moscow: Mir)
[9] Alekperov E, Reznik A 1993 Koordinatsionnaja Khimija 1 19 pp 5-14
[10] http://www.chemistry.sdsu.edu/reseach/BNMR/
[11] Kazitsyna L, Kupletskaya N 1971 Application of UV, IR and NMR spectroscopy in organic chemistry (Moscow, Vysshaya shkola)
[12] Koteneva I 2011 Boron-nitrogen surface modifiers for the protection of wood building structures (Moscow: MGSU)
[13] Temiz A, Alfredsen G, Eikenes M, Terziev N 2008 Bioresource Technology 7 99 pp 2102-2106
[14] Yalinkilic M, Gezer E, Takahashi M, Demirci Z, Ilhan R, Imamura Y 1999 Wood as raw material and material 5 57 pp 351-357
[15] Manning M 2009 30th Anniversary Of The "Moon Agreement": Retrospect And Prospects 982 pp 440–457 (USA: ACS Symposium Series)
[16] Larkin G, Merrick P, Gnatowski M, Laks P 2009 30th Anniversary Of The "Moon Agreement": Retrospect And Prospects 982 pp 458–469 (USA: ACS Symposium Series)
[17] Lomakin A 1990 Protection of wood and wood materials (Moscow: Forest industry)
[18] Akinin N, Melnikov N, Maksimenko S 2013 Vector Science, TSU 3 pp 28 – 31
[19] Leonovich A 1994 Fire protection of wood and wood-based materials (SPb: LTA)
[20] Koteneva I, Kotlyarova I, Sidorov V, Kononov G 2010 Vestnik MGSU 2 pp 198 – 203