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Complex Formation between Boric Acid and Triethanolamine in Aqueous Solutions

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The complex formation behavior between boric acid and triethanolamine (**TEA**, H_3L) in aqueous solutions was thoroughly examined by ^{11}B NMR spectroscopy. In chloroform, one ^{11}B NMR signal appeared due to triethanolamine borate (**TEA-B**, L-B) at -4.6 ppm, whereas in aqueous solutions two signals appeared due to **TEA-B** and a new boron complex at -5.8 and -9.5 ppm, respectively, in addition to a signal ascribed to boric acid and borate ion. The area ratios between the signals at -5.8 and -9.5 ppm were almost constant regardless of the molar ratios between boric acid and **TEA**, suggesting that the new complex is a 1 : 1 complex between boric acid and **TEA**. Both complexes were stable in aqueous solutions over the pH range of 6.7 to 10.9. Their chemical shift values were constant and independent of the pH value. This also implies that the new complex has a tetrahedral structure around the boron atom, similar to **TEA-B**. Based on ^{1}H and ^{13}C NMR spectroscopy and a preliminary examination of complexation between boric acid and aminoalkanols, we have concluded that the new complex (**NB**, HL-B(OH)) is a 1 : 1 boron to **TEA** complex with a bicyclo[3,3,0]structure having a boron–nitrogen bond.

We have been interested in the molecular design of novel chelating polymers for the separation of boron isotopes. The separation of boron isotopes has been attempted with anion-exchange resins,$^{1)}$ since ^{10}B isotopes are more readily fractionated to anionic $B(OH)_4{}^-$ than to neutral $B(OH)_3$ in the boron–isotope exchange equilibrium between $B(OH)_3$ and $B(OH)_4{}^-$ in aqueous solutions. This equilibrium strongly implies that ^{10}B isotopes are bound in species with a tetrahedral structure better than in those with a planar triangle structure. Thus, our attention has been focused on stable boron complexes with a tetrahedral structure around the boron atom in aqueous solutions.

Many researchers have studied the structure of triethanolamine borate (**TEA-B**, L-B),$^{2)}$ which has a tetrahedral structure around the boron atom.$^{3—6)}$ Onak et al. have shown the existence of a boron–nitrogen bond from the ^{11}B NMR spectra of **TEA-B** relatives and their hydrolysis behavior.$^{7,8)}$ The existence of a boron–nitrogen bond has also been confirmed based on X-ray structural analyses$^{9—13)}$ and photoelectron spectra.$^{14,15)}$

We examined the ^{11}B NMR spectra of **TEA-B** in two different media. Three signals were observed on the ^{11}B NMR spectra in aqueous solutions, although only one signal appeared on the spectrum in chloroform. These results show that **TEA-B** complexes partially hydrolyze. We confirmed from ^{1}H- and ^{13}C NMR spectroscopy that the hydrolysis product is a bicyclo-type complex which is formed by the opening of one NCH_2CH_2O link of the **TEA-B** molecule. This finding is in agreement with results obtained by Taylor et al.$^{16)}$ In this study, we used NMR spectroscopy to study the complex formation behaviors between boric acid and triethanolamine (**TEA**, H_3L) in aqueous solutions, and to determine the stoichiometric compositions, stability and structures of the boron complexes.

Experimental

Reagents: **TEA-B** was purchased from Tokyo Kasei. **TEA**, boric acid, diethanolamine, benzylchloride, and *N*-benzyl-2-hydroxyethylamine (guaranteed reagent grade) from Nacalai tesque were used without further purification.

***N*-Benzyl-bis(2-hydroxyethyl)amine:** A solution of diethanolamine (19.30 g, 183.6 mmol) in methanol (15 dm^3) was added to a solution of benzylchloride (26.52 g, 209.5 mmol) in methanol (35 dm^3) under reflux. After removal of the solvent, the residue was dissolved in alkaline water and extracted with ethylacetate. The extracts were washed with brine and dried. The crude product obtained after removing of the solvent was distilled under reduced pressure to obtain *N*-benzyl-bis(2-hydroxyethyl)amine (20.98 g, 58% yield). Bp 140—150 °C/0.19 kPa. ^{1}H NMR ($CDCl_3$) $\delta = 2.61$ (4H, t, $J = 5$ Hz, $NC\underline{H}_2CH_2$), 3.54 (4H, t, $J = 5$ Hz, $NCH_2C\underline{H}_2$), 3.63 (2H, s, benzyl), 4.11 (br-s, 2H, OH), 7.2—7.3(5H, m, arom.). ^{13}C NMR ($CDCl_3$) $\delta = 55.3$ ($N\underline{C}H_2CH_2$), 58.7 ($NCH_2\underline{C}H_2$), 59.0 (benzyl), 126.7 (ϕ_p), 127.7 (ϕ_o), 128.6 (ϕ_m), 138.3 (ϕ_i). MS (*m*/*z*, rel. intensity): CI (NH_3); 196 ($M^+ + 1$), EI (70 eV); 165 (13), 164 ($M^+ - CH_2OH$; 77), 92 (19), 91 (C_7H_7; 100).

NMR Measurements: We recorded the ^{1}H, ^{13}C, and ^{11}B NMR spectra at room temperature (except for the procedure which examined the influence of temperature) on a JEOL EX-400 FT-NMR spectrometer at 399.78, 100.53, and 128.26 MHz, respectively. ^{1}H and ^{13}C chemical shifts were determined with reference to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) or tetramethysilane (TMS) as an internal standard, and ^{11}B chemical shifts were determined with reference to 0.1 mol dm^{-3} boric acid D_2O solution as an external standard. We used alumina 5 mmϕ tubes (Shigemi Si-005) for samples with low concentrations of boron, in order to avoid contaminating the samples with boron contained in Pyrex sample tubes. The ^{11}B NMR spectra usually have 4096 data points over a spectral width of 4000 Hz, with a relaxation delay of 0.5 s and 1000 scans. The separation of fused peaks was carried out using computer software, MacAlice (JEOL).

Preparation of Samples: In order to obtain sample solutions with various molar ratios of boric acid to **TEA**, each 20, 60, 100, or 200 mm^3 of a 0.5 mol dm^{-3} boric acid solution was added to a mixed solution of 100 mm^3 of 1 mol dm^{-3} **TEA**, 100 mm^3 of 1 mol dm^{-3} HCl and 40 mm^3 of 1 mol dm^{-3} NaOH in a NMR tube, and diluted to a total volume of 640 mm^3 with D_2O. The NMR spectra of the samples with D_2O content of 31—59 vol% were obtained using a D_2O-lock technique.

For preparing sample solutions with various pH values, 100 mm^3 of 1 mol dm^{-3} **TEA**, 200 mm^3 of 0.5 mol dm^{-3} boric acid and 200 mm^3 of D_2O were mixed in NMR tubes, and the pH values were adjusted by adding 100 mm^3 mixtures of 1 mol dm^{-3} HCl and 1 mol dm^{-3} NaOH. The pH values were measured with a compact pH meter (Horiba B-212).

For preparing a sample solution with a pH value of 1.3, 10 dm^3 of 0.5 mol dm^{-3} **TEA-B** and 20 dm^3 of 0.5 mol dm^{-3} HCl were mixed; the mixture was diluted to a total volume of 100 dm^3 with H_2O. The NMR spectra of this sample were measured without a D_2O-lock technique.

Results and Discussion

The ^{11}B NMR spectra of **TEA-B** are shown in Fig. 1. In the chloroform system, only one signal was observed at −4.6 ppm (Fig. 1a). A pair of signals appeared on both the ^{1}H NMR and ^{13}C NMR spectra of **TEA-B** in chloroform.[17] These results show high symmetry of three ethylene chains in **TEA-B**, suggesting that **TEA-B** assumes the same structure in the chloroform solution as that in a crystalline state. The ^{11}B signal of **TEA-B** was observed at a higher frequency (−4.6 ppm), compared with those of the usual boro-ester complexes for dihydroxy compounds,[18—20] suggesting the existence of a boron–nitrogen bond in **TEA-B**. In the aqueous system, however, there are three ^{11}B NMR signals, as shown in Fig. 1b. The signal at about −3 ppm was assigned to equilibrium between boric acid and the borate ion ($\mathbf{B}/\mathbf{B}^-$), and the signal at −5.8 ppm is due to **TEA-B**. The signal at −9.5 ppm implies the formation of a new boron complex (**NB**).

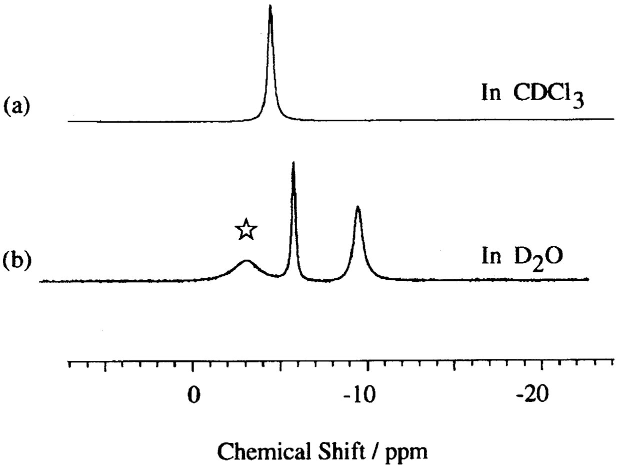


Fig. 1. ^{11}B NMR spectra of triethanolamine borate (**TEA-B**) in $CDCl_3$ at 30 °C (a) and in D_2O at 20 °C (b). The star-marked signal is due to boric acid/borate ion.

Influence of the Molar Ratio of Boron to Ligand: The ^{11}B NMR spectra of a mixture of boric acid and **TEA** in D_2O exhibit three signals, as shown in Fig. 2. The spectral pattern is the same as that of **TEA-B** in an aqueous solution (Fig. 1b). This fact shows that the complexation reaction is reversible. The chemical shifts (δ_n) and relative areas (A_n) of the signals are summarized in Table 1, where n denotes the number of signals in order of frequency. The peaks of the highest frequencies (δ_3, marked by stars in Fig. 2) are due to $\mathbf{B}/\mathbf{B}^-$, because the relative intensity (A_3) increases with an increase

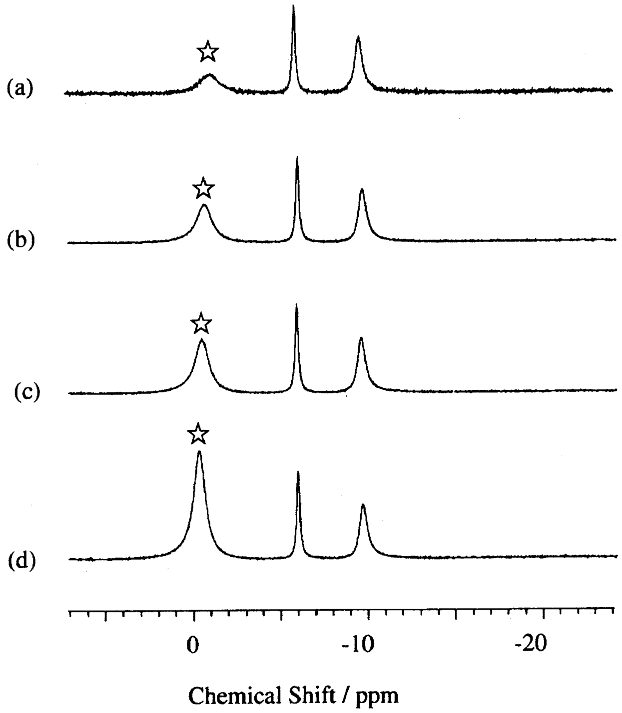


Fig. 2. ^{11}B NMR spectra of D_2O solutions containing 156 mmol dm^{-3} triethanolamine (**TEA**) and various concentrations of boric acid: 15.6 mmol dm^{-3} (a), 46.8 mmol dm^{-3} (b), 78.0 mmol dm^{-3} (c), and 156 mmol dm^{-3} (d). Star marked signals are due to boric acid/borate ion.

Table 1. Chemical Shifts (δ) and Relative Areas (A) of ^{11}B NMR Signals of D_2O Solutions Containing Boric Acid (**B**) and Triethanolamine (**TEA**) with Various Molar Ratios[a)]

TEA : **B**	pH	δ_3[b)]	A_3	δ_2[b)]	A_2	δ_1[b)]	A_1	A_1/A_2
molar ratio		ppm	%	ppm	%	ppm	%	
10 : 1	8.0	−1.1	29	−5.8	29	−9.5	42	1.5
10 : 3	7.8	−0.5	45	−5.8	23	−9.5	33	1.4
10 : 5	7.6	−0.4	51	−5.8	20	−9.5	29	1.4
10 : 10	7.4	−0.2	66	−5.8	13	−9.5	20	1.5

a) The initial concentration of **TEA** was 156 mmol dm^{-3}. The initial concentrations of boric acid were 15.6, 46.8, 78.0, and 156 mmol dm^{-3}, respectively. The measurements were performed at room temperature (about 20 °C). b) δ_n, Chemical shifts were relative to external 100 mmol dm^{-3} boric acid in D_2O.

in the initial molar ratios of boron to the ligand. The signal at -5.8 ppm can be assigned to **TEA-B** based on the agreement of its chemical shift value with that of **TEA-B** in chloroform (Fig. 1a). The formation of poly nuclear borate[21,22] hardly occurs in the boron concentration of this study. Thus, the peak at -9.5 ppm indicates the formation of a new boron complex (**NB**). The area ratio of the signal at -9.5 ppm to the signal at -5.8 ppm (A_1/A_2) is almost constant, as shown in Table 1. This suggests that **NB** is also a 1 : 1 boron to **TEA** complex similar to **TEA-B**.

Influence of pH: In order to study the stability of the boron complexes **TEA-B** and **NB**, we examined the ^{11}B NMR spectra of aqueous solutions with boric acid and **TEA** in the pH range of 1.3 to 11.7 (Fig. 3). The initial concentrations of boric acid and **TEA** were adjusted to 167 mmol dm^{-3}. The signals due to $\mathbf{B}/\mathbf{B}^-$ (marked by stars) show a lower frequency shift along with an increase in the pH value. The chemical shifts of **TEA-B** and **NB** show constant values of -5.8 and -9.5 ppm, respectively. Both complexes form in the pH range between 6.7 and 10.9; however outside this range, they hydrolyze to $\mathbf{B}/\mathbf{B}^-$, **TEA**(H_3L) and triethanolammonium ion (H_4L^+). Haveren et al. reported that the ^{11}B NMR signals of 1 : 1 boron complexes with 1, 2-dihydroxy-3-amino compounds exhibit a pH dependence in their chemical shift values.[23] These behaviors mean that such boron complexes are exchangeable with other boron complexes which form as a result of an attack of protons or hydroxide ions on the former complexes. The signals of **TEA-B** and **NB** never exhibit such a pH dependence, as shown in Fig. 3. Thus, neither **TEA-B** nor **NB** are attacked by protons or hydroxide ions. This result is suggested an existence of a boron–nitrogen bond. Thus, their complexes have stable tetrahedral structures around the boron atom.

Influence of Temperature: The ^{11}B, ^{1}H, and ^{13}C NMR spectra of 0.25 mol dm^{-3} **TEA-B** in D_2O are shown in Figs. 4, 5, and 6 respectively. The chemical shifts and relative areas of the ^{11}B NMR signals at various temperatures are summarized in Table 2. The ^{11}B signal strength due to $\mathbf{B}/\mathbf{B}^-$ increases along with an increase in the temperature (Fig. 4). This means that the complexation between boric acid and **TEA** is a exothermic reaction and occurs more extensively at lower temperatures. In Table 2, the A_1/A_2 value decreases along with an increase in the temperature. Thus **TEA-B** is more stable than **NB** at higher temperatures. In Fig. 5, all the ^{1}H NMR signals exhibit a triplet because of spin–spin couplings in ethylene chains. The coupling pairs were determined by a de-couple method and ^{1}H–^{1}H correlated spectroscopy (COSY). In Fig. 5 the coupled protons are indicated by filled and unfilled symbols of the same shape. The signals at higher frequency were assigned to *O*-methylenes, marked by unfilled symbols; the others were assigned to *N*-methylenes, marked by filled symbols. The corresponding methylene carbons are also marked by the same symbols in the ^{13}C NMR spectra (Fig. 6) based on the results of ^{13}C–^{1}H COSY. From these results, we discovered that the ^{13}C signal at 59.7 ppm is caused by an overlap of two kinds of carbons, as shown in Fig. 6.

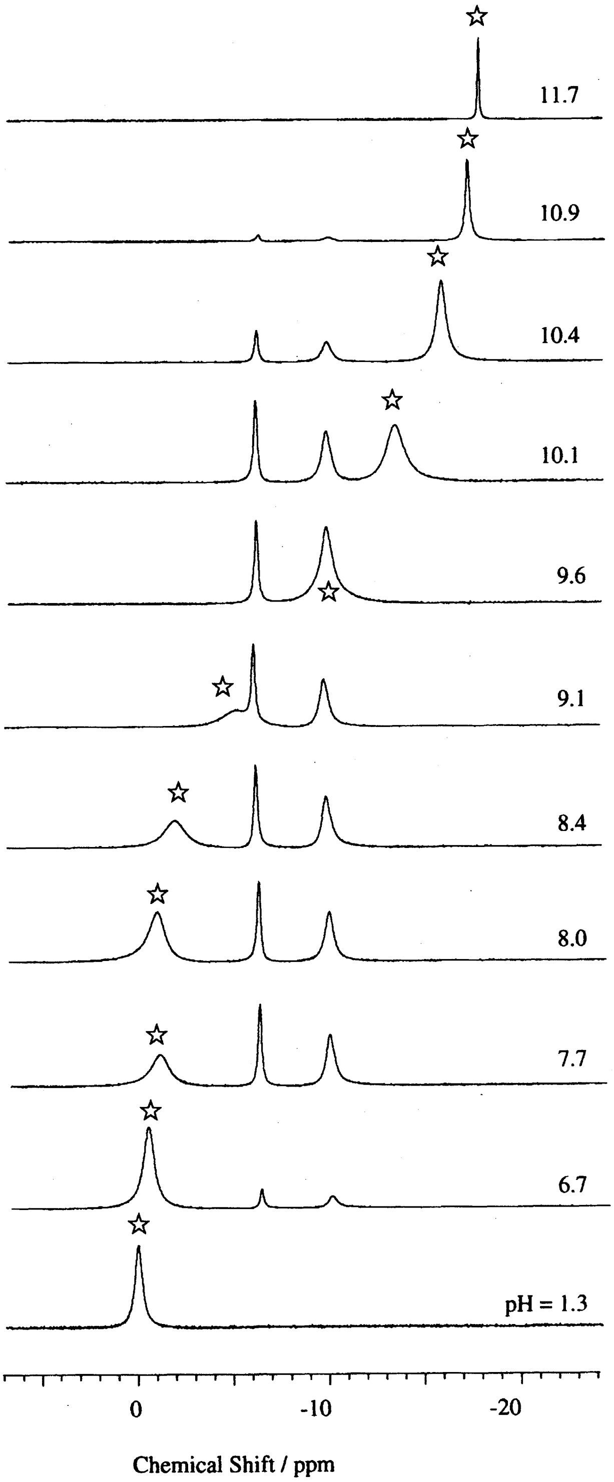


Fig. 3. ^{11}B NMR spectra of D_2O solutions containing 167 mmol dm^{-3} boric acid and 167 mmol dm^{-3} **TEA** at various pH values. Star marked signals are due to boric acid/borate ion.

There are only two pairs of signals at 90 °C in both ^{1}H and ^{13}C NMR spectra, as shown in Figs. 5a and 6a, unlike the results obtained at other temperatures. The larger pair of coupling signals in Figs. 5a and 6a are assigned to **TEA**, because $\mathbf{B}/\mathbf{B}^-$ is the main product at 90 °C based on the

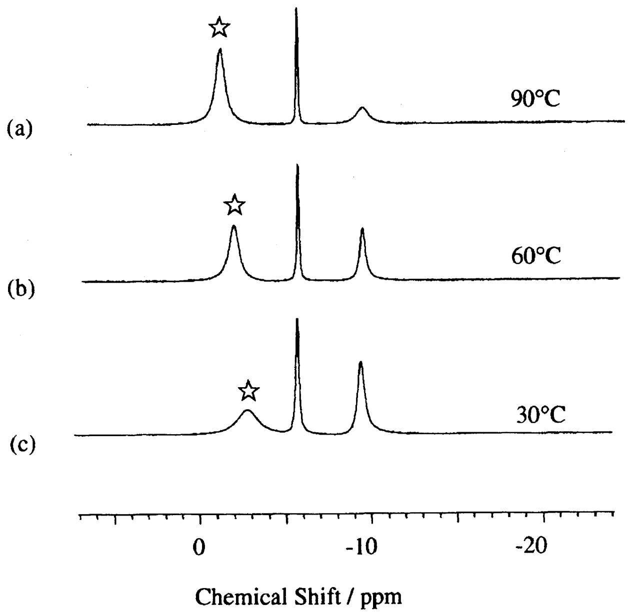


Fig. 4. ^{11}B NMR spectra of 0.25 mol dm^{-3} **TEA-B** in D_2O at various temperatures: 90 °C (a), 60 °C (b), and 30 °C (c). Star marked signals are due to boric acid/borate ion.

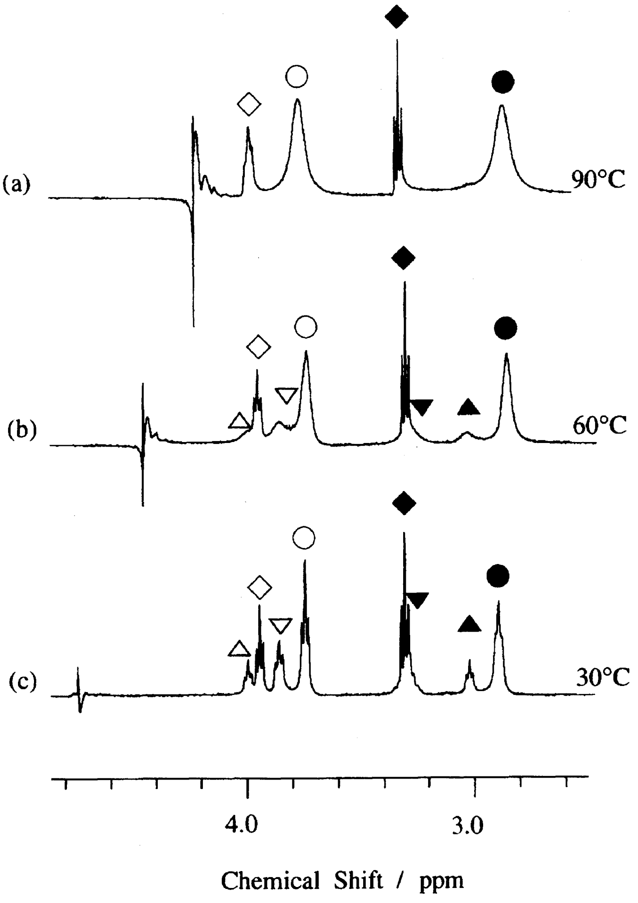


Fig. 5. ^{1}H NMR spectra of 0.25 mol dm^{-3} **TEA-B** in D_2O at various temperatures: 90 °C (a), 60 °C (b), and 30 °C (c). Each pair is marked by filled and unfilled symbols of the same shape.

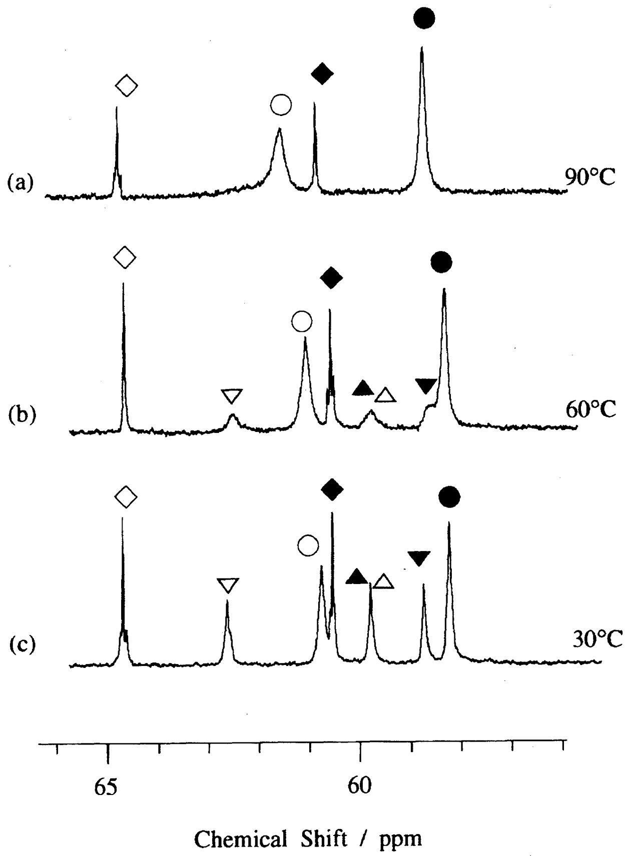


Fig. 6. ^{13}C NMR spectra of 0.25 mol dm^{-3} **TEA-B** in D_2O at various temperatures: 90 °C (a), 60 °C (b), and 30 °C (c). Each pair is marked by filled and unfilled symbols of the same shape as in Fig. 5.

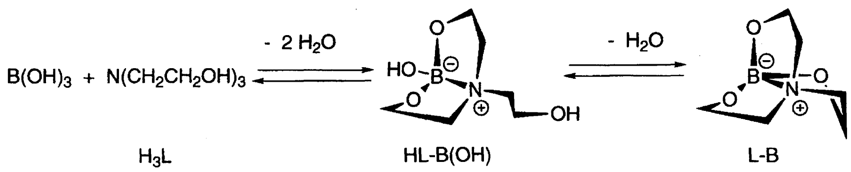
Table 2. Chemical Shifts (δ) and Relative Areas (A) of ^{11}B NMR Signals of an Aqueous Solution of Triethanolamine Borate (**TEA-B**) at Various Temperatures[a]

Temp	δ_3[b]	A_3	δ_2[b]	A_2	δ_1[b]	A_1	A_1/A_2
°C	ppm	%	ppm	%	ppm	%	
90	−0.3	65	−5.7	18	−9.5	17	0.94
60	−2.0	50	−5.7	22	−9.5	28	1.3
30	−2.9	32	−5.8	28	−9.5	39	1.4
20	−3.1	25	−5.8	30	−9.5	45	1.5

a) The concentration of **TEA-B** was 250 mmol dm^{-3}. The pH value was 8.9 at room temperature (about 20 °C). b) δ_n, Chemical shifts were relative to external 100 mmol dm^{-3} boric acid in D_2O.

^{11}B NMR spectra shown in Fig. 4a. In Figs. 5a and 6a, the other pair of signals indicate three equivalent ethylene chains derived from **TEA-B**, since the three ethylene chains of **TEA-B** are equivalent. Thus, the other two pairs of signals that disappeared at 90 °C, are assigned to **NB**, and show that **NB** has two kinds of ethylene chains. The molar ratio of these ethylene chains in **NB** is 1 : 2 from the analysis of the areas on the corresponding ^{1}H NMR signals at 30 °C.

Structure of NB: From the above results, it is clear that **NB** is a 1 : 1 boron to **TEA** complex, and has a tetrahedral



Scheme 1. Complexation equilibrium of boric acid and **TEA**.

structure around the boron atom. Accordingly, **NB** is one of the boron complexes illustrated in Fig. 7, all of which are hydrolysis products of **TEA-B**. Further, **NB** has two kinds of ethylene chains in a molar ratio of 1 : 2. To determine the structure of **NB**, we preliminary examined the complexation behaviors between boric acid and some aminoalkanols in aqueous solutions using ^{11}B NMR spectroscopy. *N*-Benzyl-2-hydroxyethylamine did not form a boron complex, but *N*-benzylbis(2-hydroxyethyl)amine formed a boron complex at -9.6 ppm in ^{11}B NMR spectra. This result suggests that the participation of more than two hydroxyalkyl groups is essential to form a stable boron complex. Thus, **NB** is a complex with an 8-membered monocyclo-structure or a 5-membered bicyclo-structure, as shown in Fig. 7. Generally, complexes with a 7-membered ring are less stable than those with a 5- or a 6-membered ring in view of an entropy effect. To the best of our knowledge, 8-membered cyclic boro-esters have not been reported so far.

According to Duin et al.,[19] as for some complexes which formed between boric acid and 1,2-dihydroxy compounds, the differences in ^{11}B chemical shifts between the 1 : 1 complex and borate ion (Δ_1) are roughly equal to those between the 1 : 2 complex and the 1 : 1 complex (Δ_2). If this rule is extended to complexes with 5-membered bicyclo systems, we can estimate the ^{11}B chemical shifts from the equation $\delta_m = -17.5+3.9\,m$, where m is the number of 5-membered rings. The values for the 5-membered bicyclo complex ($m=2$) and the 5-membered monocyclo complex ($m=1$) (illustrated in Fig. 7) are estimated to be -9.7 and -13.6 ppm, respectively.

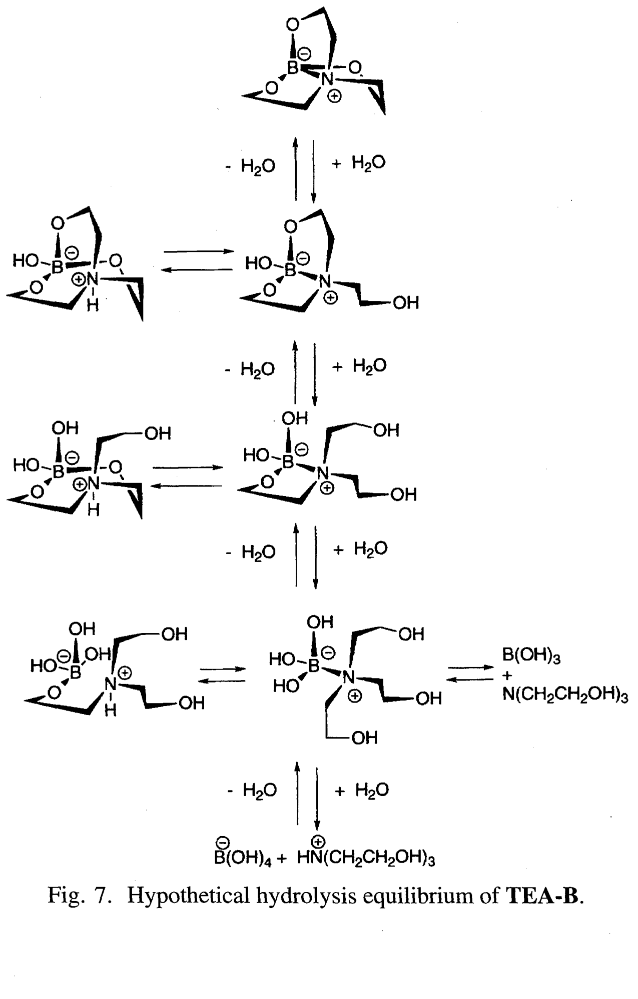


Fig. 7. Hypothetical hydrolysis equilibrium of **TEA-B**.

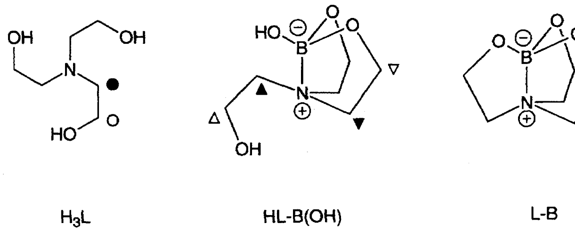


Fig. 8. Symbols assigned as per the NMR spectra.

Therefore, **NB** is a complex with a bicyclo[3,3,0] structure, which is formed by the opening of one NCH_2CH_2O link of **TEA-B**. Here, abbreviated **NB** for a new boron complex is revised to HL-B(OH) because of the meaning for the hydrolysis product of **TEA-B**(L-B). All the signals of the ^{1}H and ^{13}C NMR spectra can be satisfactorily explained by the structures of shown in Fig. 8. The complexation reactions between boric acid and **TEA**(H_3L) in aqueous solutions are described in Scheme 1.

Conclusions

We thoroughly examined the complex formation behaviors between boric acid($B(OH)_3$) and **TEA**(H_3L) in aqueous solutions based on NMR spectroscopy. In aqueous solutions, two kinds of 1 : 1 complexes were formed. They were **TEA-B**(L-B) and its hydrolysis product, HL-B(OH), with a bicyclo[3,3,0] structure. Both of them have a tetrahedral structure around the boron atom, having a boron–nitrogen bond. We believe that this is the first evidence demonstrating the existence of stable boron complexes containing a boron–nitrogen bond in aqueous solutions.

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17) Chemical shifts of **TEA-B** in chloroform (0.05 mol dm^{-3}); ^{13}C NMR $\delta = 61.9$ (CH$_2$–O), 59.3 (CH$_2$–N); ^{1}H NMR $\delta = 3.95$ (6H, t, $J = 5$ Hz, CH$_2$–O), 3.09 (6H, t, $J = 5$ Hz, CH$_2$–N).

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