^{11}B and ^{10}B NMR Investigations in Aqueous Solutions

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^{11}B NMR chemical shifts and linewidths have been measured in very dilute aqueous solutions of boric acid and borates. The results can be explained by taking pH dependent weighted averages over the species $B(OH)_3$ and $B(OH)_4^-$. The $^{11}B-^{10}B$ primary isotope effect on the magnetic shielding is smaller then $3 \cdot 10^{-8}$. The H_2O-D_2O solvent isotope effect on T_1 has been established for ^{11}B and ^{10}B in the species mentioned, and from the ratios of T_1 the quadrupolar origin of the relaxation mechanism has been inferred.

Introduction

The element boron has two isotopes which are accessible to NMR investigations: ^{11}B and ^{10}B, with natural abundances of 80.4% resp. 19.6%. There is a large amount of boron NMR investigations in boron compounds (see e.g. the reviews [1–4]), where the overwhelming majority has been performed with the nuclide ^{11}B, although the linewidths of ^{10}B are smaller by a factor of 0.65 when the relaxation mechanism is dominated by the quadrupolar interaction (see [5]; value corrected for recent data). But due to its 8.3 fold receptivity and the 2.9 fold Larmor frequency ^{11}B is favourable as to sensitivity and spectral resolution.

Surprisingly rather few investigations on aqueous solutions of boron salts are known [6–12]. The concentrations in these investigations are relatively high, and therefore extrapolation e.g. of the chemical shift to zero concentration is unreliable [10–12]. NMR investigations on very dilute aqueous solutions (concentrations < 20 millimolal) should give reliable information about the boron species present at these concentrations. This is also of importance for ^{11}B NMR studies on medical and biological fluids, which usually contain only small amounts of boron [13], and on tap and waste water [14].

In the following we report on ^{11}B (and some few ^{10}B) NMR investigations in dilute aqueous solutions of boric acid and sodium borates. Chemical shifts in their dependence on concentration and pH have been studied, as well as linewidths and longitudinal relaxation times T_1. Additionally, H_2O-D_2O solvent isotope effects and the primary $^{10}B-^{11}B$-isotope effect have been investigated.

Experimental

The ^{11}B and ^{10}B NMR investigations have been performed at 28.88 MHz resp. 9.67 MHz with a Fourier spectrometer using a Bruker SXP 4-100 console with an externally ^1H-stabilized 2.11 T Bruker magnet system. For the FID- and data-processing a B-NC 12 unit was employed. Cylindrical glass samples of 10 mm diameter have been used at a temperature of (299 ± 1) K. The boron NMR signal of the glass decays quickly and does hardly disturb the rather long free induction decay (FID) of the samples investigated. The chemical shifts are given by $\delta = (\nu_{\text{sample}} - \nu_{\text{ref.}})/\nu_{\text{ref.}}$, where as reference sample a 0.1 molal solution of $B(OH)_3$ in H_2O has been employed. For the evaluation of the T_1 values, the peak intensities of the Fourier transform inversion recovery signals have been adjusted by two- and three-parameter least squares fitting procedures [15–17]. An internal ^2H stabilization unit B-SN 20 with high resolution probes and rotating samples has been applied for the measurements of the ratios of the Larmor frequencies.

Results

Boric acid: The boron chemical shift does not depend on the concentration of boric acid in H_2O as has been reported earlier for ^{11}B [8] and ^{10}B [12] for

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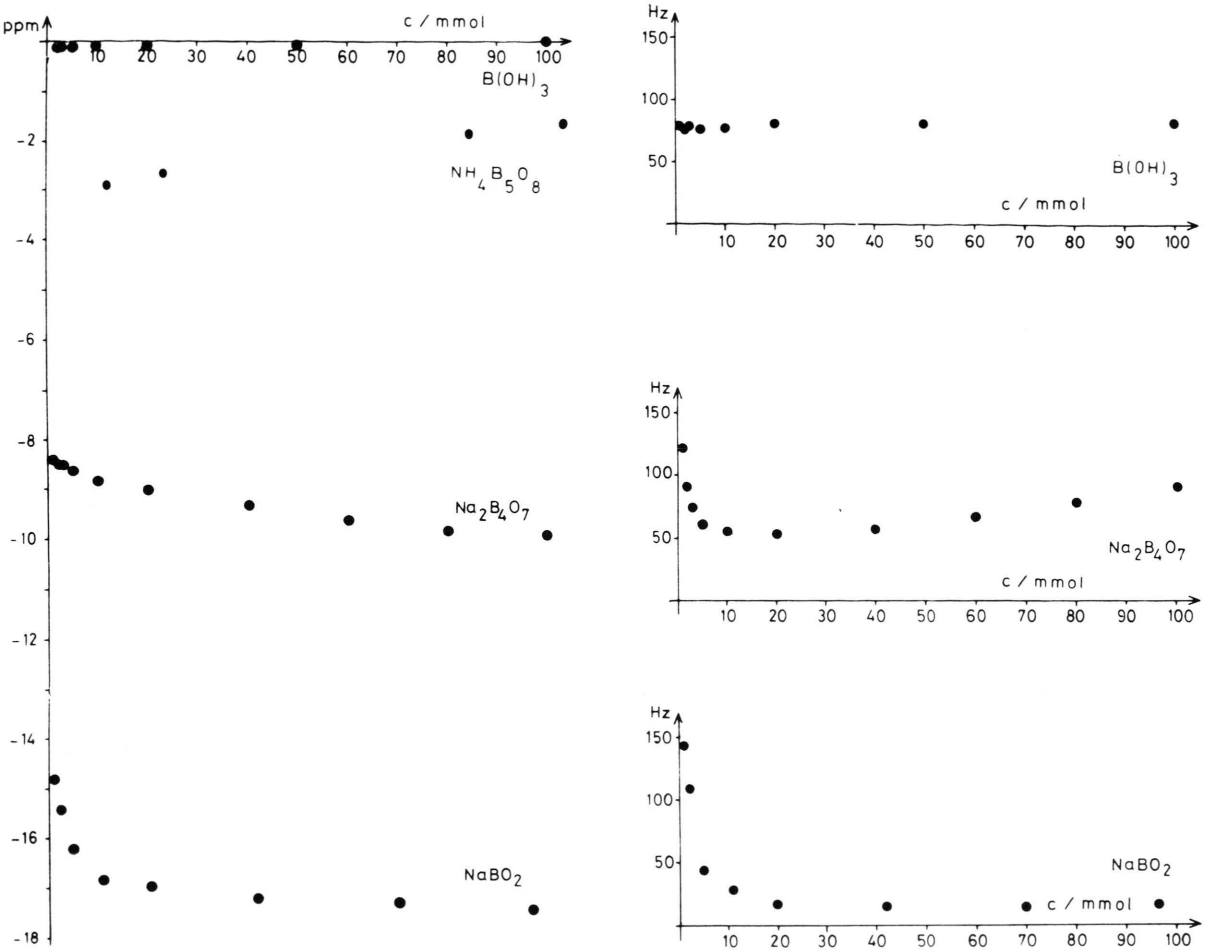

Fig. 1. Chemical shifts (left) and linewidths (right) of ^{11}B NMR signals in aqueous solutions of boric acid, sodium tetraborate, sodium borate, and ammonium pentaborate as a function of concentration. The lines especially that of $NaBO_2$ solutions at higher concentrations are broadened by the inhomogeneity of the magnetic field (non rotating samples in the high power probe).

concentrations $C > 100$ mmol. In Fig. 1 the results are presented for concentrations down to 2 mmol. Also in this range no dependence within the limits of error of ± 0.05 ppm is observable. Also the linewidths are constant for the range of 2 mmol to 500 mmol. These facts confirm earlier findings [18] that in aqueous solutions of boric acid the species $B(OH)_3$ is dominant, whereas $B(OH)_4^-$ can be neglected in the acidic range: Boric acid is a Lewis acid with a dissociation constant $K_s = 7.3 \cdot 10^{-10}$ [19] for the equilibrium

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+.$$

This is very important for solutions with higher pH, since for the resulting $pK_s \cong 9.2$ (data reported in [11] and [19] differ) the ratio $[B(OH)_4^-]/[B(OH)_3] = 1$ at pH = 9.2 for low concentrations, and the chemical shifts as well as the linewidths are very different for these two species.

In Fig. 2 chemical shifts and linewidths are presented for solutions of about 10 mmol boric acid as functions of the pH, which had been adjusted by adding HCl resp. NaOH. Between pH = 8 and pH = 10.5 a strong change in the chemical shift is observed, and at the highest pH value the chemical shift $\delta = -17.6$ ppm equals that found in aqueous

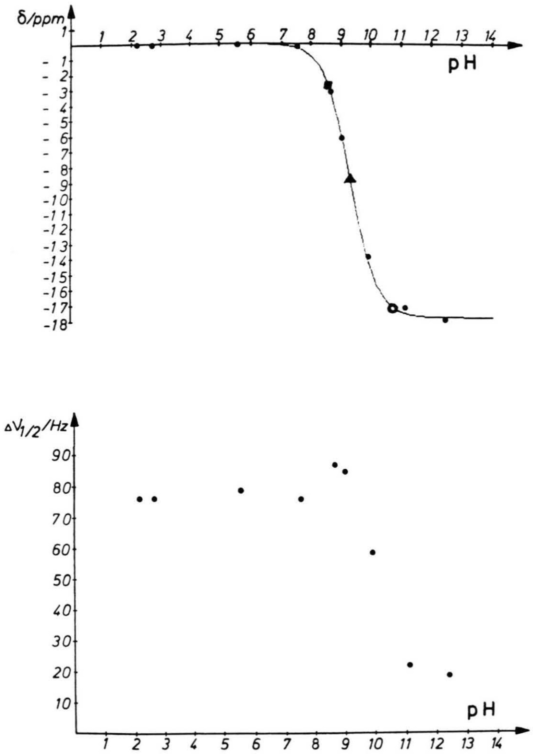

Fig. 2. ^{11}B chemical shift and linewidth of about 10 mmol solutions of $B(OH)_3$ as a function of the pH, titrated with HCl resp. NaOH: ●. δ of typical borate solutions: ■ 10 mmol $NH_4B_5O_8$, ▲ 10 mmol $Na_2B_4O_7$, ○ 10.8 mmol $NaBO_2$.

solutions of $NaBO_2$ at higher concentrations (see also Fig. 1), which means that the species $B(OH)_4^-$ is dominant. The curve given in Fig. 2 for the dependence of the chemical shift on the pH is calculated with the result of a least squares fit of $pK_s = 9.3$ by using $\delta = 0$ ppm for $B(OH)_3$ and $\delta = -17.6$ ppm for $B(OH)_4^-$. Obviously the observed chemical shift is the weighted mean of the chemical shifts of $B(OH)_3$ and $B(OH)_4^-$ due to their different concentrations as a function of pH.

The linewidth is constant in the range where $B(OH)_3$ is dominating, it decreases strongly at the pH values where the highly symmetric $B(OH)_4^-$ species becomes present. There is an interesting broadening in the transitional region from which a calculation of the exchange rate constant could be performed. But for reliable results, instead of the observed linewidths, presently not available directly measured T_2 values should be used.

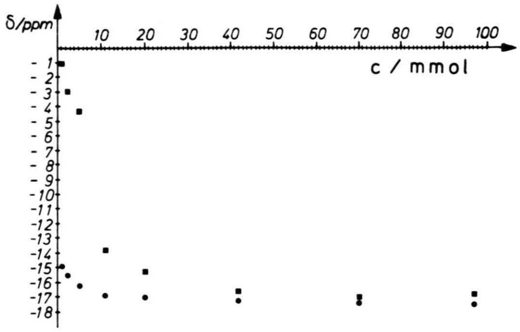

Fig. 3. Chemical shift of ^{11}B in aqueous solutions of $NaBO_2$: ● freshly prepared solutions, ■ about one year old solutions.

Sodium borate: 1 molal $NaBO_2$ solutions show a chemical shift of -17.6 ppm; the linewidth obtained with a high resolution probe is very small, about 4 Hz, which is still partly due to the inhomogeneity of the magnetic field. The results for low concentrations of $NaBO_2$ are given in Figure 1. On decreasing the concentration to about 20 mmol, δ slightly increases to -17.0 ppm. A further decrease to 1 mmol results in $\delta = -14.9$ ppm. Diminishing the concentration, which is equivalent to a decrease in the pH value from about 11.5 to 10, results in a shift of the equilibrium given above to the left side. So the observed chemical shifts and linewidths are a weighted mean of those of the species $B(OH)_3$ and $B(OH)_4^-$. The chemical shifts for the different concentrations lie accurately on the same curve as in Fig. 2, which is defined by the pK_s and pH values.

The astonishing fact, given in Fig. 3, that the chemical shift of aqueous solutions of $NaBO_2$, especially at low concentrations, is strongly time dependent can be explained in the same way. Freshly prepared samples of low concentrations from 1 mmol to 42 mmol have a pH value of 9.9 to 10.9 and are near the "critical" range. The samples which have been remeasured one year later had changed their pH to the range from 8.0 to 10.4, and so the strong time effect in the observed chemical shift is explained, an effect which for the millimolal solutions is appreciable within hours. Again all the samples lie exactly on the curve $\delta = f(\mathrm{pH})$. The linewidths (see Fig. 1) increase strongly with decreasing concentrations.

These facts are in agreement with the assumption that at higher concentrations the $B(OH)_4^-$-ion is present, and since this tetrahedral ion has a small electric field gradient at the position of the boron nucleus the NMR line is narrow whereas in the transitional region the broader line of the $B(OH)_3$ species and also the exchange broadening effects play an important role.

Sodium tetraborate: The chemical shift for the solutions of $Na_2B_4O_7$ with $100\,\text{mmol} > c > 0$ changes from $\delta = -9.9$ ppm to $\delta = -8.4$ ppm, as can be seen from Figure 1. (The shifts for the very small concentrations are also time dependent.) The pH of these solutions changes from 9.3 to 9.0. For this pH range the strongest changes in the chemical shifts (and linewidths) are expected (see Figure 2). So the chemical shift in sodium metaborate can also be explained as the weighted mean of the species $B(OH)_3$ and $B(OH)_4^-$. Adding HCl resp. NaOH to 1 mmol solutions for obtaining low resp. high pH values results in chemical shifts of 0 ppm resp. -17.6 ppm. Again the observed chemical shifts follow the relation $\delta = f(\text{pH})$.

The dependence of the linewidth on the pH is very similar for sodium tetraborate, boric acid and sodium borate.

Ammonium pentaborate: Some chemical shift results for solutions of $NH_4B_5O_8$ are given in Figure 1. A very strong and asymmetric signal is observed, changing from -1.5 ppm to -2.9 ppm with decreasing concentration. A further weak signal is found at higher concentrations, e.g. at $\delta = -18.4$ ppm for the 102 mmol solution. This signal vanishes for concentrations < 20 mmol.

Again the strong signal can be explained as the weighted average between $B(OH)_3$ and $B(OH)_4^-$: the pH increases from 7.9 for the 102 mmol to 8.5 for the 10 mmol solution. So a decrease in the chemical shift is observed for decreasing concentrations. A third signal, not resolvable due to the low magnetic field, was expected near the strong line. At 7.05 T with a Bruker CXP 300 this third signal in the 102 mmol solution has been resolved* at $\delta = -6.3$ ppm, where the intensity was about 30% of that of the strong line. This signal has also nearly vanished in the 10 mmol solution. In the literature [6, 8, 10] two or three signals are reported for solutions of alkali pentaborates with differing results. For a reliable explanation of all the signals, which are certainly due to polyanions and further exchange equilibria, a more detailed study of chemical shifts and relaxation rates at high magnetic fields in the pentaborate solutions must be performed.

Isotope effects: In NMR spectroscopy isotope effects on magnetic shielding and relaxation times can be observed. The element boron with its two rather abundant isotopes is favourable for such studies.

Primary isotope effect on magnetic shielding: The ratio of the Larmor frequencies ν of two isotopes 1 and 2 of the same element in the same magnetic field and compound is [20]

$$\frac{\nu(1)}{\nu(2)} = \frac{\gamma(1)}{\gamma(2)} \cdot \frac{(1-\sigma(1))}{(1-\sigma(2))}; \quad \begin{array}{l} \gamma\text{: gyromagnetic ratio,} \\ \sigma\text{: shielding constant.} \end{array}$$

If for two compounds having a chemical shift $\delta = \sigma_a - \sigma_b$ this ratio is not constant, there is a primary isotope effect of magnetic shielding: $\sigma(1) \neq \sigma(2)$. Only a few primary isotope effects are reported in the literature (see e.g. [20, 21]). In the case of boron some inconsistent data are available: McFarlane [22] reported the following ratios of the Larmor frequencies, obtained indirectly by the double resonance method:

$$\nu(^{11}B)/\nu(^{10}B)\{BH_4^-\} = 2.986\,317\,62(6),$$
$$\nu(^{11}B)/\nu(^{10}B)\{BF_4^-\} = 2.986\,317\,29(6),$$

where nothing is known on the origin of the error. Epperlein [23, 12] found by a direct measurement:

$$\nu(^{11}B)/\nu(^{10}B)\{B(OH)_3\} = 2.986\,318\,3(9),$$
$$\nu(^{11}B)/\nu(^{10}B)\{B(OH)_4^-\} = 2.986\,317\,6(8).$$

Further data have been obtained by measuring the Larmor frequencies of ^{10}B and ^{11}B with ^{2}H-internally stabilized high resolution probe heads [24]. 1 molal solutions of $NaBO_2$ and $AgBF_4$ in D_2O have been used, since linewidths of 1.9 Hz resp. 0.3 Hz for ^{10}B and 4 Hz resp. 0.5 Hz for ^{11}B have been achieved. The different runs of the measurements have been performed at different days with the experimental setup newly adjusted. The results are:

$$\nu(^{11}B)/\nu(^{10}B)\{B(OH)_4^-\} = 2.986\,317\,58(8),$$
$$\nu(^{11}B)/\nu(^{10}B)\{BF_4^-\} = 2.986\,317\,60(6).$$

The error is the root mean square error of the different runs. Concluding, it seems very unlikely that there is a primary isotope effect larger than $3 \cdot 10^{-8}$.

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* We thank Dr. H. Förster, Bruker Analyt. Meßtechnik, Rheinstetten, for this measurement.

Table 1. Longitudinal relaxation times of ^{10}B and ^{11}B in solutions of boric acid and sodium borate in H_2O and D_2O; mole ratio mr = mole solute/mole solvent.

Solute concentration	Boric acid mr = 0.0018		Sodium borate mr = 0.0018		Sodium borate mr = 0.018	
Species	$B(OH)_3$	$B(OD)_3$	$B(OH)_4^-$	$B(OD)_4^-$	$B(OH)_4^-$	$B(OD)_4^-$
T_1/ms of ^{11}B	5.8 ± 0.3	4.8 ± 0.2	219 ± 11	197 ± 10	121 ± 6	121 ± 6
T_1/ms of ^{10}B	9.0 ± 0.5	7.6 ± 0.4	342 ± 17	268 ± 13	175 ± 9	186 ± 9
$\frac{Q(^{10}B)}{Q(^{11}B)}$	2.07(8)	2.05(7)	2.07(7)	2.21(8)	2.15(8)	2.08(7)

An additional result is the very small boron-fluorine coupling evidenced by the narrow lines in BF_4^-:

$$J(^{10}B-^{19}F) = (0.42 \pm 0.01)\ \text{Hz} \quad \text{and}$$
$$J(^{11}B-^{19}F) = (1.23 \pm 0.03)\ \text{Hz}.$$

The ratio of the coupling constants is consistent with the ratio of the Larmor frequenices.

Solvent isotope effect: The magnetic shielding of ionic nuclei in H_2O and D_2O is often different (see e.g. [21]). In solutions of $NaBO_2$ in H_2O with a mole ratio of 0.018 the solvent isotope effect has been measured: Within the limits of error of ± 0.05 ppm no effect was observable. This is not surprising, since for ^{27}Al the effect is also very small: $\delta_{SIE} = -0.26$ ppm [25].

The exchange of the solvent H_2O by D_2O can have further consequences on the NMR signals especially in the case of quadrupolar nuclei: Due to the higher viscosity and the smaller self-diffusion coefficient of D_2O compared with H_2O, the quadrupolar relaxation of ionic nuclei shows a remarkable solvent isotope effect. In a recent review article by Holz [26] and a work by Kodweiß et al. [27] data for a couple of elements for which the effect was found are given. In Table 1 the results of measurements of the longitudinal relaxation times T_1 of ^{10}B and ^{11}B in H_2O- and D_2O-solutions of boric acid and sodium borate are listed. As expected, T_1 is short in the low symmetric $B(OH)_3$ and long for the tetrahedral $B(OH)_4^-$. Further, the typical difference for quadrupolar dominated relaxation times is found for the pairs $B(OH)_3-B(OD)_3$ and $B(OH)_4^- - B(OD)_4^-$ in the solutions with mole ratios of 0.0018 (about 0.1 mol) for ^{11}B as well as for ^{10}B. In the ten times higher concentrated $NaBO_2$ solutions the solvent isotope effect is obviously obscured by additional interactions, and further a strong decrease in T_1 is observed.

Ratio of the quadrupole moments: ^{10}B and ^{11}B have a nuclear spin quantum number of $I_{10} = 3$ resp. $I_{11} = 3/2$ and a nuclear quadrupole moment of $Q_{10} = 0.085 \cdot 10^{-28}\ \text{m}^2$ resp. $Q_{11} = 0.041 \cdot 10^{-28}\ \text{m}^2$ [28]. Applying the theory of quadrupolar relaxation of Bloembergen [29] and Hertz [30] the following relation is obtained:

$$\frac{Q_{10}^2}{Q_{11}^2} = \frac{2I_{11}+3}{2I_{10}+3} \cdot \frac{I_{10}^2(2I_{10}-1)}{I_{11}^2(2I_{11}-1)} \cdot \frac{T_1(^{11}B)}{T_1(^{10}B)}.$$

It should be mentioned that, due to the very different spin factors, ^{10}B with the larger quadrupole moment has the longer relaxation time T_1. In Table 1 the ratios of the quadrupole moments, which have been calculated from the measured T_1, are also given. These ratios are a very proof of the quadrupolar character of the relaxation since they are in agreement with the directly measured ones: Dehmelt [31] obtained from the measurement of the nuclear quadrupole resonance frequencies in solid $B(CH_3)_3$ and $B(C_2H_5)_3$ the ratio $Q_{10}/Q_{11} = 2.084 \pm 0.02$.

Acknowledgements

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