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Free Boric Acid determination in Amine Borate reaction blends using solubility studies and ^{11}B-NMR-spectroscopy

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Introduction

In September 2008, the 30th Adaptation to Technical Progress (ATP) was published in the form of a directive that amends Annex I of the Dangerous Substances Directive 67/548/EEC. As such, Boric Acid (H_3BO_3) would be listed as Category 2 reproductive toxin with risk phrases R60 and R61 ("may impair fertility and/or may cause developmental toxicity in humans"). Annex I of Directive 67/548/EEC was, however, repealed by Annex VI of the Classification, Labeling and Packaging (CLP) Regulation (1272/2008). The 30th ATP did not, therefore, come into force from 1st June 2009, but proposed for the 1st ATP into the CLP Regulation. The provisions of this 1st ATP will have to be implemented, at the latest, by 1st December 2010. As a consequence, substances containing 5.5% Boric Acid or more will be classified as toxic to reproduction, category 1B (H360FD)[1].

In November 2008, Quaker pre-registered several substances for REACh, amongst which a Mono Ethanolamine (MEA) Polyborate reaction salt. Based on new analysis techniques, the work described in this paper provides circumstantial evidence for the presence of less than 5.5% free Boric Acid ($H_3BO_{3(aq)}$) in:
a) a model reaction blend of MEA, Boric Acid and water
b) a standard semi-synthetic concentrate in which more than 5.5% of Boric Acid was incorporated.

Experimental

All experiments, including NMR spectroscopy, have been performed at 24°C (room temperature).
All ^{11}B NMR spectra have been recorded with a 300 MHz (300 DPX Bruker) spectrometer at Leiden University.

Results & discussion

Being a weak Lewis Acid, Boric Acid has the capacity to accept a hydroxide anion. The equilibrium between Boric Acid and its Boron oxo-anion is pH dependent with a pKa of 9.2[2]:

$$H_3BO_{3(aq)} + 2H_2O \leftrightarrow [B(OH)_4]^- + H_3O^+ \quad \text{[eq. 1]}$$

Depending on the concentration (> 0.025 M) and the pH, Polyborate anions are formed in the pH window of roughly 7 till 10 with the following net equations:

$$3\ H_3BO_{3(aq)} \leftrightarrow [B_3O_3(OH)_4]^- \text{ (meta borate)} + H_3O^+ + H_2O \quad \text{[eq. 2]}$$

$$4\ H_3BO_{3(aq)} \leftrightarrow [B_4O_7]^{2-} + 2H_3O^+ + 3\ H_2O \quad \text{[eq. 3]}$$

Also other poly borate anions can be formed based on B3, B4, B5 configurations or even higher molecular weight (B8).
In presence of Mono Ethanolamine (MEA) the same reaction principles can be applied resulting in the following equations:

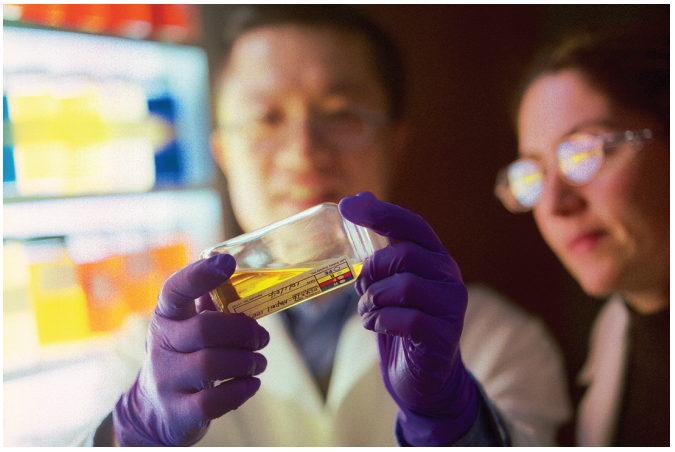
$$H_3BO_{3(aq)} + MEA + H_2O \leftrightarrow [B(OH)_4]^- [H_3NCH_2CH_2OH]^+ \quad \text{[eq. 4]}$$

$$3\ H_3BO_{3(aq)} + MEA \leftrightarrow [B_3O_3(OH)_4]^- [H_3NCH_2CH_2OH]^+ + 2\ H_2O \quad \text{[eq. 5]}$$

$$4\ H_3BO_{3(aq)} + 2\ MEA \leftrightarrow [B_4O_7]^{2-}\ 2[H_3NCH_2CH_2OH]^+ + 5\ H_2O \quad \text{[eq. 6]}$$

With these reactions in mind, a model reaction blend of 35% (w/w) demin water, 18% MEA and 47% Boric Acid was prepared in order to have an initial base/acid molar ratio (1: 2.5) between equation 5 and 6. The result was a clear solution with a pH of 8.5. Since the maximum solubility of Boric Acid in water

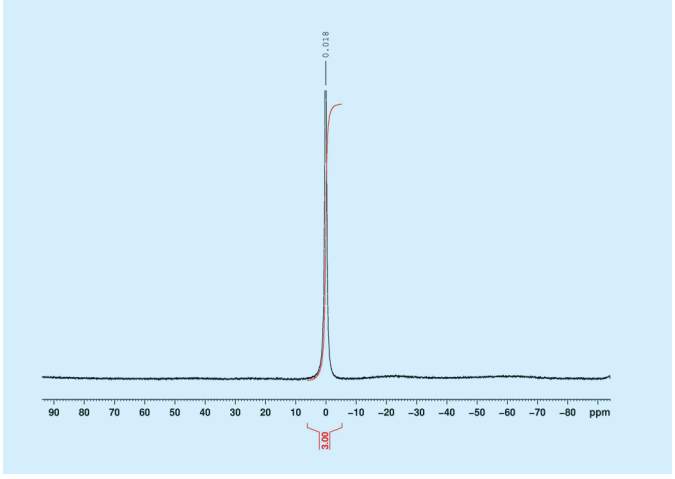
is 5.1 grams/L (24°C), this was the first indication that a reaction salt must have been formed. As such, the model reaction blend, with its 35% of demin water, should contain less than 5.5% of free $H_3BO_{3(aq)}$ in solution.



The next step in this study was to find a more analytical way for free $H_3BO_{3(aq)}$ determination. The reactions described above, however, are, to some extent, all equilibriums that shift easily during classic determinations like titration, extraction or Ion Chromatography (coupled to a mass spectrometer). In addition, the need for diluted samples will heavily influence the final determination. It was, therefore, decided to use ^{11}B NMR spectroscopy, a technique where these types of molecules and equilibriums can be detected and do not change under the influence of the applied magnetic field.

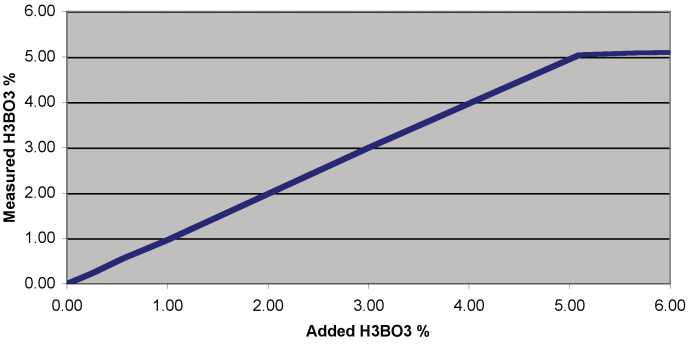
In order to quantitatively detect the amount of $H_3BO_{3(aq)}$, a calibration curve was first set up for Boric Acid solutions in demineralised water without any (pH) adjustments. These solutions, with a pH ranging from 5.4 (0.25% H_3BO_3) to 3.5 (5.1% H_3BO_3 and over saturated), showed only one very sharp peak as shown for the 3.0% (w/w) solution in *Figure 1*.

Figure 1 ^{11}B NMR spectrum of 3% Boric Acid in demineralized water



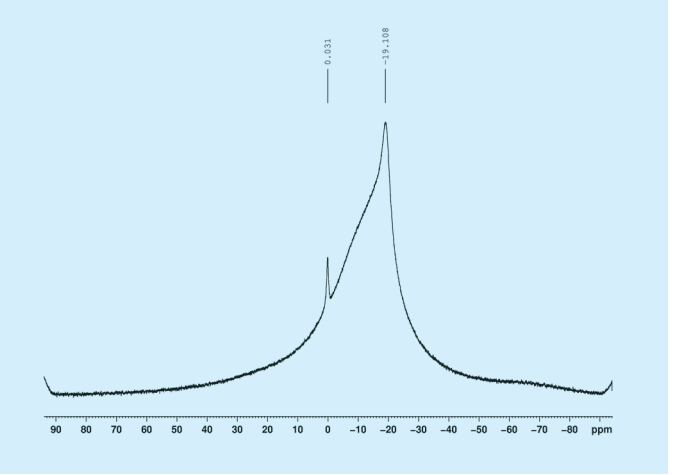
The integrals of these peaks (chemical shift set on 0 ppm) plotted against the amount of Boric Acid (w/w %) showed an excellent linear correlation up to 5.09% *(Figure 2)*. At higher concentrations, the integral does not increase since the maximum solubility was reached.

Figure 2 Calibration curve $H_3BO_{3(aq)}$ quantification by ^{11}B NMR spectroscopy



In the next step, the model reaction blend was determined in combination with an internal capillary - containing a separate 3% (w/w) Boric Acid solution - as external reference. The sharp reference peak at 0 ppm ($H_3BO_{3(aq)}$) was indeed visible (*Figure 3*), however, the presence of $H_3BO_{3(aq)}$ in the reaction blend could not be proven due to the large and broad peak. Several dilutions of this reaction blend were, therefore, determined. *Figure 4* indicates that the curve of the pure solution is a combination of only two peaks, clearly without having an overlap with the $H_3BO_{3(aq)}$ peak at 0 ppm.

Figure 3 ^{11}B NMR spectrum of model reaction blend (undiluted) with external reference



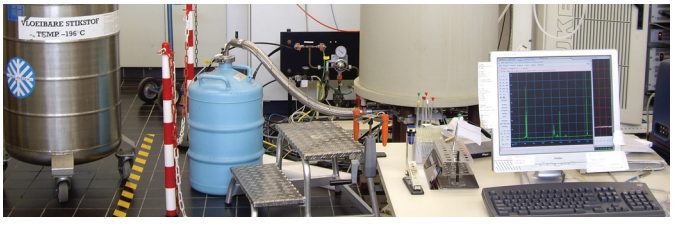
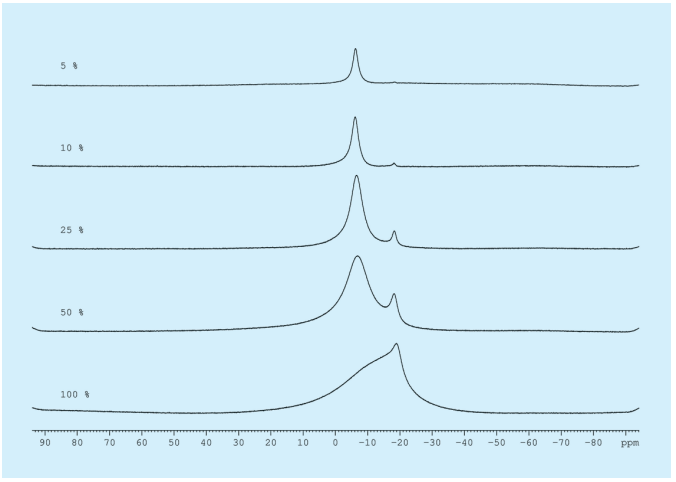
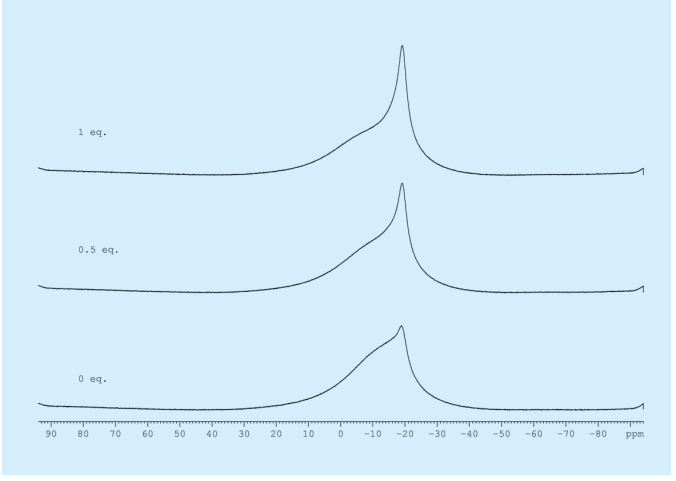


Figure 4 ^{11}B NMR overlap spectrum of model reaction blend and dilutions thereof



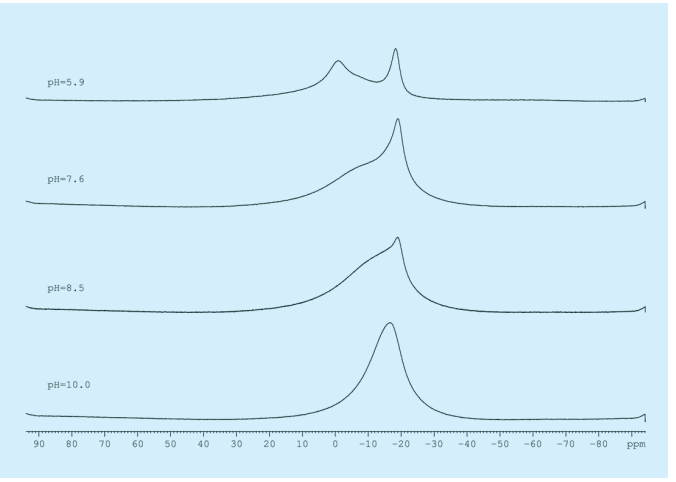
The evidence that the undiluted reaction blend hardly contains $H_3BO_{3(aq)}$ is further supported by the observation that 0.5 extra equivalents Boric Acid (9.5%, w/w) can still be dissolved completely without giving precipitation. In addition, the $H_3BO_{3(aq)}$ signal remained absent in the spectrum (*Figure 5*). Addition of 1 equivalent of Boric Acid, however, could not be dissolved completely anymore, but still did not introduce the $H_3BO_{3(aq)}$ peak in measurements that were performed on part of the clear top layer.

Figure 5 Effect of Boric Acid addition on ^{11}B NMR spectrum (overlap) of model reaction blend (undiluted)



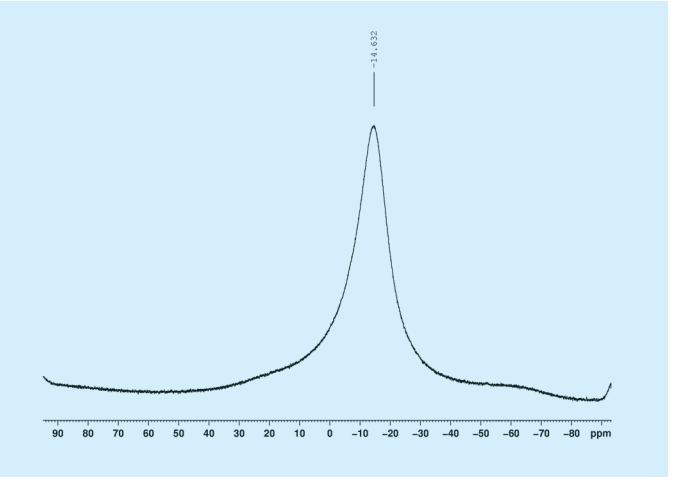
In order to shift the equilibrium towards $H_3BO_{3(aq)}$ or a sharper MEA Polyborate peak, the pH of the undiluted reaction blend was adjusted with a minimum of KOH or HCl solution as depicted in *Figure 6*. From this, it can be concluded that $H_3BO_{3(aq)}$ is not present at pH 10, whereas the $H_3BO_{3(aq)}$ peak is clearly present at pH 5.9.

Figure 6 Effect of pH on ^{11}B NMR spectrum (overlap) of model reaction blend (undiluted)



Finally, a standard semi-synthetic Machining & Grinding concentrate was prepared where significantly more than 5.5% of Boric Acid was incorporated by means of the model reaction blend. *Figure 7* shows a single peak – less broad than the model reaction blend - for this undiluted product. A separate sharp $H_3BO_{3(aq)}$ peak is clearly not visible, indicating that a fully formulated Machining & Grinding fluid based on the incorporation of large amounts of Boric Acid does not necessarily lead to more than 5.5% free Boric Acid ($H_3BO_{3(aq)}$).

Figure 7 ^{11}B NMR spectrum of semi-synthetic coolant (concentrate)



It has not been our purpose to identify and quantify every individual peak in the NMR spectra, however, several researchers have reported their findings on the qualitative (3D) characterization of Amine (Poly) Borates with other techniques like ^{1}H NMR spectroscopy and X-ray Crystallography[3,4]. Nevertheless, quantification of impure poly borates with these techniques still seems very difficult.

Conclusion

The results of this study[5] show that it is very difficult or even impossible to determine the exact amount of $H_3BO_{3\,(aq)}$ in undiluted reaction blends of MEA, Boric Acid and water. Summarizing all facts and measurements, however, it is concluded that there must be clearly less than 5.5% $H_3BO_{3(aq)}$ present in the model reaction blend. Based on the amount of $H_3BO_{3(aq)}$ being less than 5.5% in this reaction blend, it is reasonable to assume that this does not result in a classification toxic to reproduction from 1st December 2010. The (repro-) toxic properties of MEA Polyborates in solution, however, are not yet completely known and will be mapped in subsequent toxicological studies the coming years as part of the full REACh registration process.

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5) This study has been presented during meetings of the VSI/VKIS (November 2008), UKLA (January 2009) and UEIL (January 2009)

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