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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 Annex I of Directive 67/548/EEC was, however, repealed by Annex VI of the Classification, Labeling and Packaging (CLP) Regulation (1272/2008).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