Capacity Enhancement of Aqueous Borohydride Fuels for hydrogen storage in liquids

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Abstract

In this work we demonstrate enhanced hydrogen storage capacities through increased solubility of sodium borate product species in aqueous media achieved by adjusting the sodium (NaOH) to boron (B(OH)₃) ratio, i.e., M/B, to obtain a distribution of polyborate anions. For a 1:1 mole ratio of NaOH to B(OH)₃, M/B = 1, the ratio of the hydrolysis product formed from NaBH₄ hydrolysis, the sole borate species formed and observed by ¹¹B NMR is sodium metaborate, NaB(OH)₄. When the ratio is 1:3 NaOH to B(OH)₃, M/B = 0.33, a mixture of borate anions is formed and observed as a broad peak in the ¹¹B NMR spectrum. The complex polyborate mixture yields a metastable solution that is difficult to crystallize. Given the enhanced solubility of the polyborate mixture formed when M/B = 0.33 it should follow that the hydrolysis of sodium octahydrotriborate, NaB₃H₈, can provide a greater storage capacity of hydrogen for fuel cell applications compared to sodium borohydride while maintaining a single phase. Accordingly, the hydrolysis of a 23 wt% NaB₃H₈ solution in water yields a solution having the same complex polyborate mixture as formed by mixing a 1:3 molar ratio of NaOH and B(OH)₃ and releases >8 eq of H₂. By optimizing the M/B ratio a complex mixture of soluble products, including B₃O₃(OH)₅²⁻, B₄O₅(OH)₄²⁻, B₃O₃(OH)₄⁻, B₅O₆(OH)₄⁻ and B(OH)₃, can be maintained as a single liquid phase throughout the hydrogen release process. Consequently, hydrolysis of NaB₃H₈ can provide a 40% increase in H₂ storage density compared to the hydrolysis of NaBH₄ given the decreased solubility of sodium metaborate.

Key words: liquid hydrogen storage, solubility, polyborate mixtures.

1. Introduction

The US DoE Fuel Cell Technologies Office recently released a new set of hydrogen storage metrics and targets for non-vehicular applications ranging from materials handling equipment, e.g., fork lifts and airport tugs, to portable power equipment (PPE), e.g., battery chargers and Unmanned Aerial Vehicles.¹ Specifically, the new gravimetric (40 g H₂/kg system) and volumetric (50 g H₂/liter system) hydrogen storage targets for single charge PPE present new opportunities for materials discovery. One approach that has a strong appeal for both PPE and vehicular applications are liquid carriers.²⁻⁹ Liquid hydrogen carriers offer attractive options for hydrogen storage materials given their ease of transfer to and from devices using pumps and pipes in existing infrastructure, as well as ease of transfer within devices (e.g., from a storage tank to a reactor).

Hydrolysis of borohydrides and ammonia borane has been investigated to evaluate the potential of aqueous liquid carriers.¹⁰⁻¹³ Aqueous sodium borohydride (SBH) in particular has been researched extensively¹⁴ as a liquid hydrogen carrier because it is highly soluble in water (360 g/L) with a theoretical gravimetric capacity of 7.3 wt.% H₂:

However, a major shortcoming in the NaBH₄ approach is the failure to remain liquid *throughout the entire hydrogen release cycle* at high loadings since additional water is required to keep the sodium metaborate hydrolysis product soluble. The Hydrogen-on-Demand, HOD®, system was developed for vehicular applications using 20-30 wt.% solutions of NaBH₄ (ca. 4-6.5 wt% hydrogen on a material basis). Anything greater than 20 wt.% NaBH₄, i.e., 4.5 wt% H₂, presents a challenge to maintain a single liquid phase because of the solubility limit of sodium metaborate (SMB) and led to the DOE curtailing research on aqueous NaBH₄ for vehicular applications.

Starting with the known solubility of hydrolysis product: i.e, 590 g (5.8 moles) NaB(OH)₄ in a 1 liter saturated solution at 60 °C one can work backward to determine the quantity of extra water that is required to maintain a liquid phase starting from SBH and ending with SMB. This approach shows that the aqueous solution needs to ‘provide or carry’ a minimum 3.5 extra

equivalents of water to keep the products in solution at 60 °C, corresponding to a maximum hydrogen capacity of 4.6 wt.% as illustrated in equation 2.

It is notable that 1 liter of solution containing 590 g NaB(OH)_4 remains a liquid yet only yields 4.6 wt% H_2 . The challenge thus lies in approaches to prepare solutions of borates that will remain soluble on scales $> \sim 600$ g of a borate salt in a saturated solution.

A survey of the literature shows that the solubility of sodium borates varies dramatically as a function of the Na/B ratio (Fig. 1).¹⁵ At 60 °C there is a maximum solubility near Na/B = 0.31. The reason for this is that there is not a simple borate anion formed to charge-balance sodium; instead a complex mixture of polyborate anions is formed through a series of condensation equilibria:¹⁶

Our hypothesis is that this mixture of borate anions will not readily undergo a phase change during the reaction and minimize or delay crystallization through an inverse corollary of the common ion effect. We therefore considered borohydrides where the Na/B ratio is close to the 0.31 maximum in Figure 1. There are a large number of boron hydrides species,^{17,18} however, the candidates with the most potential include $\text{Na[B}_4\text{H}_9]$ (Na/B = 0.25) and $\text{Na[B}_3\text{H}_8]$ (Na/B = 0.33).

Shore and co-workers have recently shown that hydrolysis of sodium octahydrotriborate, NaB_3H_8 provides 9 equivalents of H_2 .^{19,20} Furthermore they note that aqueous solutions of NaB_3H_8 are more stable than aqueous solutions of NaBH_4 , a desirable feature for practical hydrogen storage carriers. Based on our analysis of sodium polyborate solubility, we suggest that the hydrolysis of NaB_3H_8 can be carried out under concentrated conditions; i.e., only 2 extra equivalents of water are required:

This corresponds to a 23 wt.% solution of NaB_3H_8 in water and a hydrogen capacity of 6.5 wt.%. Hypothetical BO_2^- and H^+ are shown in this equation for simplicity, but in practice the hydrolysis products will contain the polyborate anions shown in equations 3 and further water will be generated in condensation reactions to aid solubility. Thus we anticipate increased solubility of both the polyborate hydrolysis products and the NaB_3H_8 , which has a reported aqueous solubility of 74 wt. %.

In this report we test the hypothesis of the ‘*reverse engineering*’ approach by confirming the solubility of the corresponding polyborate hydrolysis products for a ratio of $\text{Na/B} = 1/3$ by preparing surrogate products from 1 to 3 stoichiometric mixtures of NaOH and B(OH)_3 and measuring hydrogen release from aqueous solutions of NaB_3H_8 at concentrations necessary to deliver 6.5 wt% H_2 from a liquid fuel.

2. Materials and methods

2.1 Synthesis of NaB_3H_8 : Solvent-free NaB_3H_8 was synthesized according to a published literature procedure.²¹ A Na/Hg amalgam was reacted with $\text{THF} \cdot \text{BH}_3$ under nitrogen to form NaBH_4 and NaB_3H_8 . After removal of THF and redissolution in diethyl ether, NaBH_4 was removed by filtration. The filtrate was concentrated under vacuum to an oil from which NaB_3H_8 precipitated upon addition of dichloromethane. Approximately 4.5 g of the white powder was recovered by filtration and vacuum drying. It is notable that Titov has reported the preparation of a variety of cationic octahydrotriborates, i.e., lithium, potassium, magnesium, calcium and strontium, as solvates of dioxane or diglyme,²² while Chong et al. have prepared the unsolvated $\text{Mg(B}_3\text{H}_8)_2$ by a diborane-free pathway by thermal decomposition of $\text{Mg(BH}_4)_2$.²³

2.2 Solubility measurements: A surrogate solution of the corresponding polyborate solution expected to be formed in the hydrolytic decomposition of NaB_3H_8 were prepared from 1 to 3 stoichiometric mixtures of NaOH and B(OH)_3 in various amounts of ‘excess’ water. For example to simulate the product solution from the reaction of 7.50 g NaB_3H_8 (0.118 mol) with 21.28 g reactant H_2O (1.18 mol) with 4.12 g excess water that would yield 6.5 wt% H_2 , 4.12 g H_2O , 4.73 g NaOH , and 21.9 g B(OH)_3 were added in the order listed to a 3-neck flask with

magnetic stirrer and temperature controller set at 60 °C. The mixture readily formed a clear mobile solution. [*Caution: the reaction of NaOH with B(OH)₃ is rather exothermic*]. This solution was maintained with stirring at 60 °C for 24 h and remained crystal clear.

2.3 Hydrogen measurements from catalytic hydrolysis of NaB₃H₈: Under an atmosphere of N₂, a 5 mL round bottom flask was charged with sodium triborane (56.2 mg, 0.885 mmol), equipped with a Schlenk adapter, and capped with a rubber septum. The reaction vessel was then connected to a gas burette which included a condenser to prevent moisture contributing to the measurement of gas released. An aqueous solution of 0.253 M CoCl₂, prepared under ambient conditions, was then added (180 µL, 0.0455 mmol, 5.1 mol%) to the reaction vessel. The mixture rapidly released hydrogen and precipitated cobalt nanoparticles. The amount of hydrogen released was found to be 8.7 equivalents in 2 minutes. After no more hydrogen evolved, the mixture was analyzed by ¹¹B NMR spectroscopy. All of the sodium triborane had been consumed, and the remaining material was a mixture of borates. ¹¹B NMR (H₂O, 160 MHz): 17-11 (br), 0.97 (s) ppm.

3. Results and Discussion

Aqueous solutions of the spent fuel compositions of NaBH₄ (Na/B = 1) and NaB₃H₈ (Na/B ≈ 0.33) were prepared to verify whether their hydrolysis products remained soluble under the expected conditions of a hydrogen delivery system. Solid reagents were first dissolved in water at 60 °C and allowed to cool to room temperature. The results are summarized in Table 1, which confirms the greater solubility of products for Na/B ≈ 0.33. The hydrogen contents for the corresponding aqueous liquid fuels are also shown in Table 1, calculated using the relationships given in Equations 1 and 4. Note that at this stage of analysis we are focusing on product stability and are therefore using theoretical rather than measured hydrogen contents. The Na/B = 1 solutions remained clear up to 5.0 wt. % H₂, but showed undissolved solids at 5.2 wt% H₂. By contrast, the Na/B ≈ 0.33 solutions were transparent at 5.4 wt% H₂ and still stirrable, though viscous, at 6.7 wt% H₂. A photograph of the polyborate solution simulating release of 6.35% H₂ (Na/B = 0.34) is shown in Figure 2 after cooling to room temperature. No precipitation was observed and the solution remained easily stirrable. These results show that more boron-rich sodium borohydride compounds are likely to provide higher hydrogen-containing fuels than

NaBH₄; and in particular that NaB₃H₈ is a strong candidate for aqueous fuels containing greater than 6 wt.% H₂.

Hydrogen release was measured from a concentrated (23 wt.%) NaB₃H₈ solution, which corresponds to the composition described by Eq 4. The solution was injected into a flask at room temperature containing 5 mol% CoCl₂ as a pre-catalyst. The results (Fig. 3) showed a rapid release of 8 equivalents of H₂, corresponding to a hydrogen generation rate of 1 gs⁻¹ for a 1L reactor. The fluctuations in the curve before 1 minute including the overshoot past 8 equivalents are a consequence of the heat released from CoCl₂ reduction and hydrogen release, which caused gas expansion more rapidly than could be compensated by the burette's thermocouples.²⁴ The total H₂ measured is less than the 9 equivalents or 6.5 wt.% of H₂ expected theoretically by equation 4. The difference is due to some of the B₃H₈⁻ being used to generate the active Co nanoparticle catalyst from CoCl₂. Although reduction using B₃H₈⁻ has not been extensively studied, comparison with the more widely used BH₄⁻ suggests that each M²⁺ ion results in one fewer H₂ molecule and the maximum hydrogen expected from our experiment is therefore 8.5 equivalents.²⁵ Once the catalyst has been reduced, subsequent hydrolyses are likely to deliver the expected 6.5 wt.% H₂. Since the engineering requirements for generating hydrogen from a liquid at room temperature are relatively modest, this provides a good basis for meeting the system target of 4.5 wt.% H₂.

¹¹B NMR spectroscopy of the hydrolysis products showed broad peaks corresponding to a range of different products (Figure 4), which is consistent with our hypothesis of multiple polyborane anions. The peaks at +18, +13, and +1 ppm can be assigned to B(OH)₃/B(OH)₄⁻, B₃O₃(OH)₄⁻, and B₅O₆(OH)₄⁻ respectively.^{16,26} The peaks are broadened because of rapid exchange between the different borate sites in the polyborate anions. The tetraborate dianion, B₄O₅(OH)₄²⁻, and triborate dianion, B₃O₃(OH)₅²⁻, give very broad resonances which are not observed in ¹¹B NMR spectra. None of the starting NaB₃H₈ remained, which has a characteristic 9-line resonance near -31 ppm.

4. Conclusions

In this work we described a rational approach to determine the ‘practical’ hydrogen storage capacity, i.e., the hydrogen storage capacity of a liquid material that remains liquid throughout, by determining the most soluble polyborate solution as a function of the sodium to boron ratio.

This reverse engineering approach, i.e., starting with the most soluble mixture of polyborate anions and working backward to choose the corresponding borohydride provides an approach to maximize the hydrogen storage capacity of a liquid phase borohydride carrier. The greatest solubility occurs when the ratio of Na/B is between 0.25 – 0.35 as a result of (i) a mixture of polyborate products that are formed resulting in meta-stable solutions with slow crystallization kinetics and (ii) condensation reactions that produce water to replace the water that is consumed to generate hydrogen. We show that hydrolysis of a 23 wt% solution of NaB_3H_8 provides a liquid carrier capacity of 6.5 wt% hydrogen. Further work to investigate the solubility of other ionic polyborates, e.g., Li, NH_4 , Mg, Ca, could lead to the discovery of other octahydroborates that could further increase the hydrogen storage capacity while maintaining a liquid phase from beginning to end. This work teaches that it is advantageous to obtain a mixture of products to optimize solubility and minimize unwanted crystallization of highly concentrated solutions of boron hydride hydrolysis products.

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¹ See section 3.3 Hydrogen Storage in the Fuel Cell Technologies Office Multi-Year Research, Development, & Demonstration Plan - <http://energy.gov/sites/prod/files/2014/03/f12/storage.pdf>

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Figures and Tables

Table 1. Aqueous sodium borate solutions representing spent fuel at various concentrations. The wt. fraction H₂ is calculated for the corresponding borohydride solutions.

NaOH (g)	B(OH) ₃ (g)	H ₂ O, (g)	Na/B	Wt .frac H ₂	Appearance
31.65	48.93	45.5	1.0	4.82%	Clear
31.65	48.93	41.0	1.0	4.99%	Clear
31.65	48.93	35.2	1.0	5.22%	Solids
4.82	21.99	11	0.34	5.40%	Clear
4.82	21.9	5	0.34	6.35%	Cloudy
4.7	23.25	3.2	0.31	6.74%	Viscous, but stirrable

Figure 1. Plot of solubility of sodium polyborate solutions (B_2O_3) as a function of $Q = Na/B$ ratio. The highest solubility of borates is between $Q = 0.25$ and 0.33). At $Q = 1$, e.g., hydrolysis of $NaBH_4$ to yield $NaB(OH)_4$ solubility limit at $60\text{ }^\circ\text{C}$ is ca. 20 wt% B_2O_3 compare to $Q = 0.31$ where solubility is ca. 40 wt% B_2O_3 .

Figure 2. Aqueous sodium polyborate solution ($\text{Na/B} = 0.34$) simulating spent fuel after release of 6.35 wt.% H_2 cooled to room temperature.

Figure 3. Hydrogen release from a 23 wt.% solution of NaB_3H_8 with 5 mol% CoCl_2 catalyst, measured by gas burette at room temperature.

Figure 4. (A) ^{11}B NMR spectrum of NaB_3H_8 hydrolysis products, broad peak centered $\sim +15$ ppm is due to mixture of polyborate products, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_5\text{O}_6(\text{OH})_4^-$, peak at $+2$ ppm is $\text{B}(\text{OH})_4^-$. (B) ^{11}B NMR spectrum of NaB_3H_8 starting material before addition of catalyst showing characteristic nonet at -31 ppm due to coupling with eight equivalent hydrogens.