Modeling of Self-Hydrolysis of Concentrated Sodium Borohydride Solution

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Abstract

In spite of the US DOE recommendation of no-go for sodium borohydride for on-board vehicular hydrogen storage, a great deal of interest remains particularly with view to portable applications. In this work we report on experimental and modeling studies of the kinetics of self-hydrolysis of concentrated $NaBH_4$ solutions (10 – 20 wt %) for temperatures varying between 25 – 80 ^{0}C, based on ^{11}B NMR study. The models studied were a power law model and a model which describes the change in order of borohydride during the course of reaction. The modeling results show an increase in rate constant and decrease in the order of reaction with respect to borohydride with temperature, while reverse trends are observed with increasing initial borohydride concentration. A theoretical analysis based on solubility product constant for precipitate formation is also carried out under the studied experimental conditions and is in good agreement with the experimental observation.

1. Introduction

Sodium borohydride hydrolysis, being well within the 2015 targets, regarding specific energy and energy density, falls short in practice due to the low efficiency of the water-based system. The excess water necessary to drive the reaction, the stabilization of sodium borohydride by the production of basic species in the course of the reaction, as well as water capture by the by-products, are factors known to decrease the gravimetric efficiency and which limits the use of concentrated solutions [1-6].

$NaBH_4$ undergoes self-hydrolysis even at room temperature, when it is mixed with water and depends on pH, temperature, and initial borohydride concentrations [7]. Therefore, successful handling and storing of $NaBH_4$ solution would require the knowledge of self-hydrolysis kinetics. Despite extensive efforts, the kinetics and

mechanism of self-hydrolysis is not fully understood. This work attempts to model the self-hydrolysis of concentrated borohydride solutions based on ^{11}B NMR studies.

2. Experimental

The self-hydrolysis experiments were performed taking as a base on an NMR study, where metaborate is the by-product. The intensities of the borohydride and metaborate were taken with a Varian Inova 500 spectrometer operating at 160.487 Hz for [11]B. The capacity of the NMR machine is in the temperature range of 25 - 90 ^{0}C with an accuracy of ± 0.1 ^{0}C. The concentrations of the borohydride and metaborate are quantified from the NMR intensities with reference to the standard boric acid solution and are used in the modeling study. Solutions varying from 10 to 20 wt % and temperatures varying from 25 - 80 ^{0}C were studied for a reaction time span of 25 hours.

3. Modeling of Self-Hydrolysis of NaBH$_4$

It has been visually observed that under the studied experimental conditions, no precipitates have been formed. An analysis based on solubility product constant has been carried out to confirm theoretically the above experimental observation. The objective is to get an insight into the stoichiometry of the reaction and thereby fixing the stoichiometry in the modeling studies.

The concentration of anhydrous metaborate (NaBO$_2$) for precipitation to occur in varying concentrations of borohydride solutions and at different temperatures, calculated using solubility product constant of NaBO$_2$ is given in Table 1. As seen from column 4 and 5, the concentration of NaBO$_2$ required for precipitation is higher than the measured NaBO$_2$ concentration under all experimental conditions, implying no precipitation, which is observed experimentally

Table 2 shows the concentration of hydrated metaborate (NaBO$_2$.xH$_2$O) for precipitation to occur in varying concentrations of borohydride solutions and at different temperatures. The change in x with temperature, i.e., x = 4 below 53.6 ^{0}C and x = 2 from 53.6 ^{0}C to 105 ^{0}C is incorporated in the calculation. As seen from column 4 and 5, the measured metaborate concentration under all cases is higher than the concentration for precipitation to occur and it should precipitate if the metaborate is in the hydrated form. However, no precipitate is formed under these conditions shows the evidence of the absence of hydrated metaborates.

The hydrolysis reaction is then assumed to occur under the following reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad\qquad (1)$$
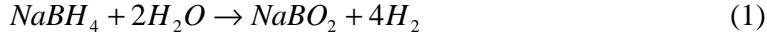
The initial kinetic model is described by a power-law model in borohydride concentration:

$$-\frac{dNaBH_4}{dt} = \frac{dNaBO_2}{dt} = k[NaBH_4]^n \qquad\qquad (2)$$

Where, k is the rate constant, and n is the order of reaction with respect to sodium borohydride.

On the basis of the work of Davis et al. [7], Gonçalves et al. [8] described the reaction, for 10 wt% borohydride solutions at temperatures between 300 and 363K, by an empirical correlation with two terms, expressing separately the contributions of the acidic and the basic conditions. A good agreement between experimental and simulated data was obtained, with the term including the proton predominating at low pH and the water term at high pH.

The assumption now made that water concentration is constant and that the acidic term can be neglected, as reflected in equation 2, seems justified given the large excess water and basicity in all tests undertaken.

The kinetic parameters were estimated by gPROMS parameter estimation tool box [9]. The model prediction using the estimated parameters is compared with measurements in figure 1. As seen from figure 1, there is a good agreement between the prediction and measurements. The kinetic parameter estimated and the statistical test on the parameters in terms of confidence interval, 95 % t-value, standard deviation and 95 % reference t-value is given in Table 3 (columns 3-4) and Table 4 respectively. As seen from Table 4, the estimated kinetic parameters are statistically very significant.

There is a variation of kinetic parameters with initial borohydride concentration and temperature as evident in Table 3. The rate constant decrease and the order of reaction with respect to borohydride concentration increase with initial borohydride concentration, which is opposite to increase in temperature. Also, the magnitude of the order of reaction is very high, implying self-hydrolysis reaction occurring by multi steps. Therefore, in the present study, work has also been carried out using a simple model (equation 3), which occur by more than one step and describes change in order of reaction with respect to borohydride concentration.

$$-\frac{dNaBH_4}{dt} = \frac{dNaBO_2}{dt} = \frac{k_1 C^m{}_{NaBH_4}}{1 + k_2 C^n{}_{NaBH_4}} \qquad\qquad (3)$$

Where k_1 and k_2 are rate constants and m and n are orders with respect to borohydride concentration. This model we referred as Model 2.

The two extreme possibilities of Model 2 are:

1. At high concentration of $NaBH_4$, the order is m-n with respect to $NaBH_4$.

2. At low concentration of $NaBH_4$, the order is m with respect to $NaBH_4$.

The kinetic parameters are estimated using gPROMS similar to power law model and the estimated parameters are also given in Table 3 (columns 5 - 8) for comparison with the parameters estimated by power law model. Comparing column 3 and column 9 (m-n for Model 2) shows that for borohydride concentration varying from 10 – 20 wt % and at 25 ^{0}C, m-n of Model 2 corresponds to n of power law model, implying high concentration of $NaBH_4$. However, at higher temperature, parameter m of Model 2 (column 5) equals n of power law model (column 3), implying high concentration of $NaBH_4$. This can be explained as follows: increase in temperature increases the rate of reaction which decreases the $NaBH_4$ concentration during the course of reaction.

Comparison of prediction using Model 2 with measurements is also illustrated in Figure 1. As seen, there is a good agreement between model prediction and measurements similar to the case of power law model.

4. Conclusions

Modeling of self-hydrolysis of $NaBH_4$ has been carried out using experimental data based on ^{11}B NMR. Power law model with respect to borohydride concentration and a model which describes change in reaction order of borohydride concentration are compared using gPROMS. The study confirms that self-hydrolysis occur by step-wise mechanism. Identification of all self-hydrolysis reaction products and the development of a kinetic model is the subject of future work.

References

[1] Marrero-Alfonso EY, Beaird AM, Davis TA, Matthews MA. Hydrogen generation from chemical hydrides. Ind Engg Chem Res 2009;48(3):3703-3712.

[2] Pinto AMFR, Falcao DS, Silva RA, Rangel CM. Hydrogen generation and storage from hydrolysis of sodium borohydride in batch reactors. Int J Hydrogen Energy 2006; 31:1341-1347.

[3] Wee JH, Lee KW, Kim SH. Sodium borohydride as the hydrogen supplier for proton exchange membrane fuel cell systems. Fuel Process Technol 2006;87:811-819.

[4] Liu BH, Li ZP. A Review: Hydrogen generation from borohydride hydrolysis reaction. J Power Sources 2009;187:527-534.

[5] Demirci UB, Akdim O, Miele P. Ten-year efforts for sodium borohydride for on-board automotive hydrogen storage, Int J Hydrogen Energy 2009;34:2638-2645.

[6] Schlesinger HI, Brown HC, Finholt AE, Gilbreath JR, Hoekstra HR, Hyde EK. Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen, J. Am. Chem. Soc 1953; 75:215-219.

[7] Davis R. E.,E. Bromels, C. L. Kibby, 1962, Boron Hydrides. III. Hydrolysis of Sodium Borohydride in Aqueous Solution, J. Am. Chem. Soc. 84, 885-892.

[8] Gonçalves, A., Castro, P., Novais, A.Q., Fernandes, V., Rangel, C. and Matos, H., Dynamic Modeling of Hydrogen Generation via Hydrolysis of Sodium Borohydride, In Proceedings of PRES'07, 24-28 June, Ischia, Italy, (In Chemical Engineering Transactions, Vol. 12, 2007. Editor: Jiri Klemes, AIDIC, Italy, 243.)

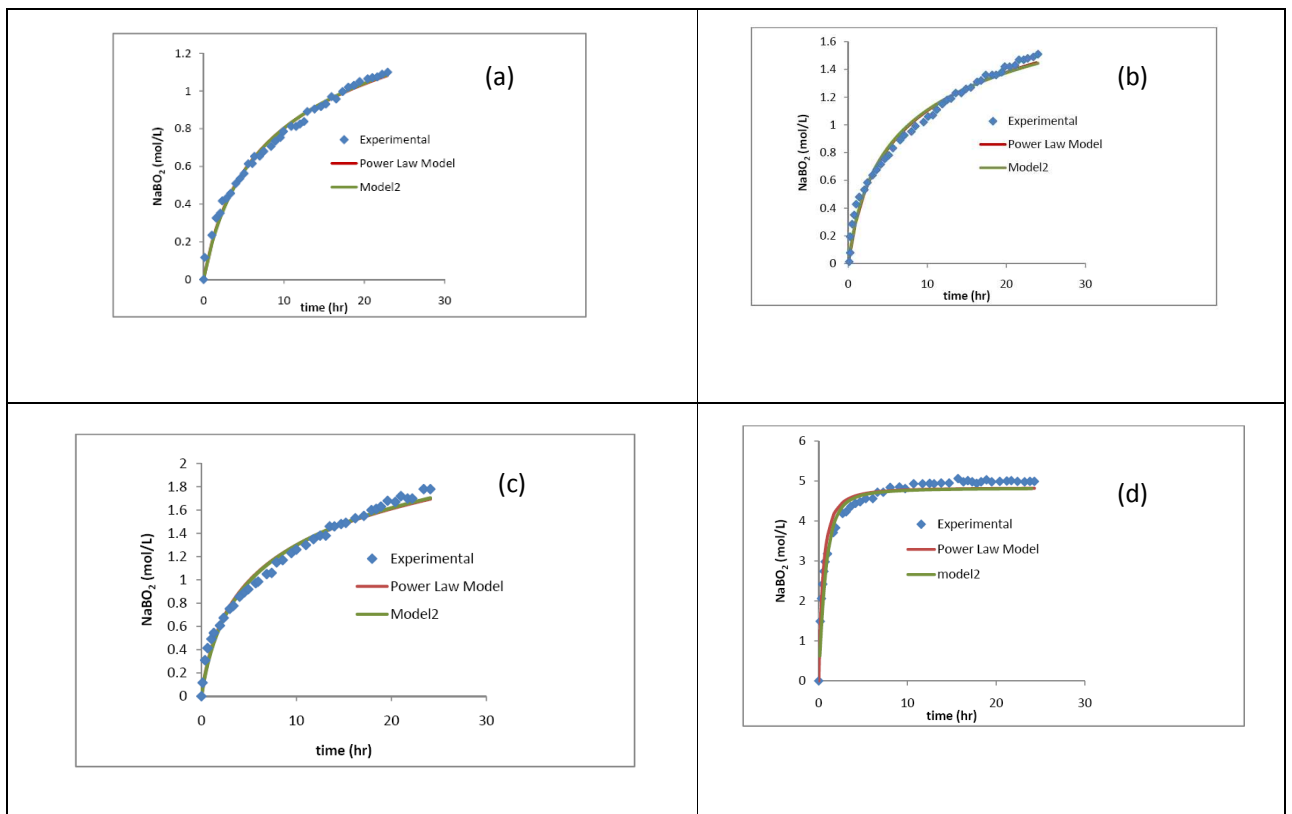[9] gPROMS Advanced User Guide, 2004, Process Systems Engineering

Fig.1. Comparison of measurements with model prediction. (a) 10 wt % $NaBH_4$ at 25 ^{0}C; (b) 15 wt % $NaBH_4$ at 25 ^{0}C; (3) 20 wt % $NaBH_4$ at 25 ^{0}C (4) 15 wt % $NaBH_4$ at 80 ^{0}C.

Table 1. Solubility product constant, saturated concentration of $NaBO_2$ for precipitation and experimental metaborate concentration with temperature and borohydride concentration.

T (^{o}C)	$NaBH_4$ (wt %)	K_{SP}	C_{NaBO2} (M) for precipitation	Metaborate concentration (M) (Experimental)
25	10	14.28	2.67	1.12
25	15	14.28	2.27	1.54
25	20	14.28	1.95	1.75
25	15	14.28	2.27	1.54
60	15	53.26	5.57	4.46
80	15	80.92	7.21	5.3

Table 2. Solubility product constant, saturated concentration of $NaBO_2.xH_2O$ for precipitation and experimental metaborate concentration with temperature and borohydride concentration.

T (^{o}C)	NaBH$_4$ (wt %)	K$_{SP}$	C$_{Na(BOH).XH2O}$ (M) for precipitation	Metaborate concentration (M) (Experimental)
25	10	4.6	1.193	1.12
25	15	4.6	0.932	1.54
25	20	4.6	0.753	1.75
25	15	14.28	0.932	1.54
60	15	53.26	3.09	4.46
80	15	80.92	3.58	5.3

Table 3. Estimated kinetic parameters for power law model and model 2.

T (°C)	NaBH$_4$ (wt %)	n (Power law model)	k (Power law model	m (Model 2)	n Model 2)	k$_1$ (Model 2)	k$_2$ (Model 2)	m-n (Model 2)
25	10	6.2734	5.41e-04	3.6034	-2.716	0.061452	214.03	6.3194
25	15	9.314	1.14e-06	6.7232	-3.1912	3.617e-5	212.96	9.9144
25	20	12.593	4.25e-10	9.1123	-3.1214	4.067e-8	464.25	12.2337
60	15	2.2551	6.41e-02	2.1581	0.48637	0.47994	3.8124	1.67173
80	15	1.67	8.07e-01	1.7353	0.59184	4.114	3.733	1.4346