

4-15-2014

Kinetic Modeling of Self-Hydrolysis of Aqueous NaBH₄ Solutions by Model-Based Isoconversional Method

Rajasree Retnamma

A. Q. Novais

C. M. Rangel

Lin Yu

Michael A. Matthews

University of South Carolina - Columbia, mamatthe@mailbox.sc.edu

Follow this and additional works at: https://scholarcommons.sc.edu/eche_facpub

 Part of the [Chemical Engineering Commons](#)

Publication Info

Published in *International Journal of Hydrogen Energy*, Volume 39, Issue 12, 2014, pages 6567-6576.

© International Journal of Hydrogen Energy 2014, Elsevier.

Retnamma, R., Novais, A.Q., Rangel, C.M., Yu, L., & Matthews, M.A. (2014). Kinetic Modeling of Self-Hydrolysis of Aqueous NaBH₄ Solutions by Model-Based Isoconversional Method. *International Journal of Hydrogen Energy*, 39 (12), 6567-6576.

<http://dx.doi.org/10.1016/j.ijhydene.2014.02.035>

This Article is brought to you by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.

Kinetic modeling of self-hydrolysis of aqueous NaBH₄ solutions by model-based isoconversional method

Rajasree Retnamma^{a,*}, A. Q. Novais^a, C. M. Rangel^{a,*}, Lin Yu^b, Michael A. Matthews^b

^a National Laboratory of Energy and Geology (LNEG), Estrada do Paço do Lumiar 22, Lisbon 1649-038, Portugal

^b Department of Chemical Engineering, Swearingen Engineering Centre, University of South Carolina, 301 South Main Street, Columbia, SC 29208, USA

Highlights

- Established the NaBH₄ self-hydrolysis kinetics by model-based isoconversional method
- Apparent reaction order decreases with temperature irrespective of extent of conversion
- Apparent activation energy increases with extent of conversion
- Experimental results are in good agreement with the model predictions

Abstract

The present work reports the kinetic modeling of self-hydrolysis of non-buffered, non-stabilized NaBH₄ solutions by model-based isoconversional method. The overall kinetics is described by a ‘reaction-order’ model in a practical operating window of 10–20 wt% NaBH₄ solutions at 25–80 °C and 0–50% conversions. The apparent activation energy and pre-exponential factor are interrelated through a kinetic compensation effect (KCE). The apparent reaction order remains constant at a given temperature irrespective of extent of conversion and decreases with increase in temperature. It decreases from first-order to 0.26 with increase in temperature from 25 to 80 °C. The apparent activation energy is found to increase from 65 ± 11 to 162 ± 2 kJ mol⁻¹ with increase in extent of conversion from 0 to 50%. The variation of parameters with extent of conversion is discussed based on changes in solution properties during the progress of hydrolysis reaction.

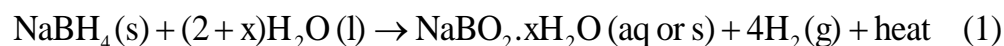
Keywords: Sodium borohydride, Self-hydrolysis, Kinetics, Isoconversional method, Hydrogen production

Corresponding author Tel.: +351 210924657; fax: +351 217166568

E-mail addresses: r_rajasree@yahoo.com, agosto.novais@lneg.pt, carmen.rangel@lneg.pt, YU@email.sc.edu, MATTHEWS@cec.sc.edu

1. Introduction

Sodium borohydride (NaBH₄) undergoes self-hydrolysis in the presence of water while generating hydrogen according to [1–3]:



where x is the excess hydration factor [2].

The overall conversion of this reaction at room temperature is 7-8% [4-5], making it inappropriate for a practical H_2 generator. Certain metal catalysts accelerate the reactant conversion and metal-catalyzed hydrolysis is being accepted as a potential technology for delivering H_2 to portable fuel cells [6-9]. While the conversion of $NaBH_4$ is accelerated by metal-catalyzed hydrolysis, self-hydrolysis still occurs to some extent at low temperatures and becomes significant at elevated temperatures. This needs to be arrested for increasing the shelf-life of the reactant solution [10-14].

There are also unresolved issues such as the minimization of the amount of water and the nature of hydration of metaborate by-products which limit the net or usable hydrogen storage capacities [2]. An alternative method, steam or water-vapor hydrolysis can enhance the net hydrogen storage capacities without catalyst, if operating conditions are optimized [15-17]. Self-hydrolysis of concentrated $NaBH_4$ solutions at high temperature is one of the important steps in the steam or water-vapor hydrolysis reaction pathway. Therefore, the knowledge of the self-hydrolysis kinetics of concentrated $NaBH_4$ solutions at high temperature is important for liquid-phase catalytic hydrolysis (handling and storage of borohydride solutions) and developing steam or water-vapor hydrolysis technology.

The rate dependence of pH and mechanistic details of self-hydrolysis were extensively studied in 1960s and 1970s [18]. These studies were in controlled buffer solutions (7.7-14 pH) and reported various models based on pH range. These models were established under highly diluted solutions of $NaBH_4$ (< 0.4 wt%) at low to medium temperatures (15-35 °C) and for low percentages (< 5%) of $NaBH_4$ conversion. These conditions are not suitable for practical applications. Also, aqueous $NaBH_4$ solutions become more basic during self-hydrolysis and cannot be described by the rate expressions in buffered solutions, which maintain constant pH during the progress of reaction [18].

Self-hydrolysis kinetics of non-buffered, non-stabilized $NaBH_4$ solution were reported in the 2000s by various authors [14, 19-20, 22]. Moon et al. [14] investigated experimentally the effects of $NaBH_4$ concentration (5-25 wt%) and temperature (25-45 °C) of the hydrolysis reaction on the hydrogen generation rate and yield. Their results imply the occurrence of different hydrolysis kinetics for diluted and concentrated solutions, which is thought to be attributed to the reduction in water activity as a result of increasing solution viscosity.

Gonçalves et al. [19] developed a five-step mechanistic model for fairly concentrated solution (10 wt%) at 45 °C. The same authors, in another study [20] extended it to 65 °C with the addition of a modified version of the Davis et al. [21] empirical correlation. Even though these studies showed a reasonably good agreement in the case of generated H_2 volume, there is a mismatch between experimental and model predicted pH values, particularly during the initial stage of the hydrolysis reaction, where the increase in pH is quite rapid and crucial in terms of H_2 production. This points to the additional computation based on modified model.

Andrieux et al. [22] studied the self-hydrolysis kinetics of 2.3-18.9 wt% solutions at temperatures of 30-80 °C. The kinetic parameters were estimated as a function of extent of conversion assuming constant

reaction order with temperature. Apparent activation energy of $98 \pm 10 \text{ kJ mol}^{-1}$ and a zero-order in NaBH_4 concentration was found for 20 and 40% conversions. However, the R^2 values obtained for order of reaction are 0.66 and 0.61, implying a low quality fit and hence to uncertainty in the reported zero-order reaction rate. A more detailed analysis based on extent of conversion by relaxing the assumption of constant reaction order with temperature is required to gain additional insights into the mechanism.

Recently, two models were reported for self-hydrolysis kinetics of stabilized NaBH_4 solutions with particular focus on storage applications. The first model by Churikov et al. [23] for highly stabilized (12–14.0 pH) diluted to medium concentrated NaBH_4 solutions (0.5–7 wt%) at medium to high temperatures (50–100 °C) comprises two parts depending on pH range. One part represents the high pH range where the hydrolysis rate is independent of pH, and the other part represents the reduced pH range where the hydrolysis rate increases with decrease in pH. This model exhibits some limitations, namely, the first-order in borohydride is not consistent over the whole time range, and the reaction order exceeds unity (1.79) in hydrogen ion concentration. The second model derived from extensive experimental kinetic data (stabilized 0.5–25 wt% NaBH_4 , 7.7–13.0 pH, 25–75 °C) by Bartkus et al. [24] consists of two semi-global rate equations. The first reaction describes the rate of consumption of NaBH_4 . The second reaction, which is the major contribution of this study, describes the rate of depletion of hydrogen ion. This complex model depends on extent of conversion and initial borohydride concentration could well describe the hydrolysis kinetics only at higher solution pH values.

From this literature survey, it is clear that there is no reported model so far to describe the NaBH_4 self-hydrolysis kinetics in a wide practical operating window. Development of a model that can describe the self-hydrolysis kinetics of non-buffered, non-stabilized solutions in a wide practical operating window (10–20 wt% NaBH_4 , 25–80 °C, 0–50% conversions) is the objective of the present work. Isoconversional methods are often used to describe complex heterogeneous kinetics, particularly for solid-state reactions [25–27]. This isoconversional method does not require a detailed reaction mechanism and computes apparent activation energy as a function of the extent of conversion and has been shown to produce consistent kinetic results from isothermal and non-isothermal experiments. However, the isoconversional method assumes a single (but unspecified) reaction mechanism that is invariant during the progress of reaction and not affected by the change in temperature. Based on the extensive prior work, it is likely that the mechanism of NaBH_4 self-hydrolysis changes during the progress of reaction and also with temperature [18]. In the present work, we employ a model-based isoconversional method that has the potential to capture the change in reaction mechanism during the progress of reaction as well as with change in temperature or temperature regime.

2. Modeling

Isoconversional model

The kinetics of complex heterogeneous processes that are stimulated by change in temperature (T), is generally expressed as a function of T and extent of conversion α [25–28]:

$$\frac{d\alpha}{dt} = \phi(T, \alpha) \quad (2)$$

The single-step kinetic approximation assumes the function ϕ as a product of two separable functions independent of each other as [29]:

$$\phi(T, \alpha) = k_{\text{ap}}(T) f(\alpha) \quad (3)$$

where t is the time, $k_{\text{ap}}(T)$ the apparent rate constant depends on T , and $f(\alpha)$ the conversion function representing the process mechanism. While assuming single-step kinetics (eq 3), a complex set of kinetic equations describing the multi-step process is treated as a single-step kinetic equation and the rate constant obtained is thus an apparent constant [30–32].

The isoconversional method by single-step kinetic approximation is then obtained by combining eqs 2 and 3:

$$\frac{d\alpha}{dt} = k_{\text{ap}}(T) f(\alpha) \quad (4)$$

Equation 4 implicitly assumes that the conversion function $f(\alpha)$ holds throughout the reaction process and the mechanism of the process is solely a function of conversion and independent of any temperature or temperature regime [28–29]. The reaction rate at constant extent of conversion is thus only a function of temperature and allows the estimation of the apparent activation energy as a function of α .

There is a high possibility that, $f(\alpha)$ the function representing the mechanism of the process does not hold neither throughout the hydrolysis reaction, nor with changes in temperature during the complex NaBH_4 self-hydrolysis process. The present work attempts to address this issue by employing a model-based isoconversional method, which has the potential to capture the change in mechanism of the process throughout the process as well as with temperature or temperature regime.

The NaBH_4 hydrolysis process exhibits its maximum rate at the beginning of the reaction, which decreases continuously with the extent of conversion [14, 22]. The most appropriate form of $f(\alpha)$ for such decelerating type process is the ‘reaction-order model’ and is assumed to be of the form [27]:

$$f(\alpha) = (1 - \alpha)^m \quad (5)$$

where m is the apparent reaction order.

The rate expression for model-based isoconversional method assuming single-step kinetic approximation is obtained by combining eqs 4 and 5:

$$\frac{d\alpha}{dt} = k_{\text{ap}}(T) C_0^{m-1} (1-\alpha)^m \quad (6)$$

where C_0 is the initial reactant concentration.

The explicit temperature dependence of the rate constant, $k_{\text{ap}}(T)$, follows an Arrhenius relationship:

$$k_{\text{ap}}(T) = A_{\text{ap}} \exp\left(\frac{-E_{\text{ap}}}{RT}\right) \quad (7)$$

where E_{ap} is the apparent activation energy, A_{ap} the apparent pre-exponential or frequency factor, and R the gas constant.

The activation energy and pre-exponential factor are generally assumed to be constant with the extent of conversion. However, they can vary for both elementary and complex reactions [25-27]. The change in the apparent activation energy (E_{ap}) with α is described by [33–34]:

$$E_{\text{ap}} = \varepsilon_0 + \varepsilon_1 \ln(1 - \alpha) \quad (8)$$

The dependence of apparent activation energy on apparent pre-exponential factor is computed by the following kinetic compensation effect (KCE) relationship [35–38]:

$$\ln A_{\text{ap}} = \alpha^* + \beta^* E_{\text{ap}} \quad (9)$$

where α^* , β^* , ε_0 and ε_1 are constants. Equation 9 implies that any change in the apparent activation energy E_{ap} is compensated by the change of A_{ap} .

3. Parameter estimation solver

The estimation of the five parameters (α^* , β^* , ε_0 , ε_1 and m) is performed by the parameter estimation tool of gPROMS software (PSE Enterprise, London, UK). The MXLKHD solver based on maximum likelihood approach is used, where the global optimum is found by applying a sequential quadratic programming (SQP) method. The MXLKHD solver calls the DASOLV solver for the solution of the kinetic model comprising the differential algebraic equations. A constant variance model, i.e. the measurement error with constant standard deviation is determined as part of optimization. Besides rapid estimation of the parameters, the powerful numerical method provided by gPROMS allows rigorous statistical testing of the estimated parameters for uncertainty in the values and the model validation of how good the model responds to the system.

4. Experimental

The experimental kinetic data used in the present study are those reported by Yu and Matthews [39]. The evolution of metaborate formation and NaBH_4 consumption were characterized *in-situ* by ^{11}B nuclear magnetic resonance (NMR) technique for non-buffered, non-stabilized NaBH_4 solutions. The experiments were carried out on 1.6 mL 10–20 wt% solutions at 25–80 °C. The details of experimental runs, in terms of duration of the experiments and conversion at the end of the experiments are given in Table 1.

As seen in Table 1, the final conversion increases with operating temperature and decreases with initial NaBH₄ concentration. This is in agreement with Moon et al. [14] for the hydrolysis of non-buffered, non-stabilized NaBH₄ solutions of 5–20 wt% at low to medium temperatures (25–45 °C). These authors determined conversion by measuring hydrogen evolution from a jacketed batch reactor with 100 g solution. The quantitative comparison of conversions of Moon et al. [14] with Yu and Matthews [39] is only possible at 25 °C (the only temperature covered by both studies), at which temperature there is a reasonable agreement. The favorable comparison of the kinetic data despite the use of different types of experiments supports the reliability of values of the estimated parameters in the present work.

5. Results and discussion

5.1. Parameter estimation

The objective was to estimate the parameters for a reasonable level of conversion and investigate the effect of extent of conversion on the estimated parameters. The approach involved the estimation of α^* , β^* , ϵ_0 , ϵ_1 and m at various temperatures for a pre-defined conversion using different initial NaBH₄ concentrations. This demands experimental conversions above the pre-defined conversions at each temperature on different initial concentrations of NaBH₄. As seen in Table 1, 20 wt% NaBH₄ solutions at 25 °C gives 24% conversion, implying maximum possible conversion for parameter estimation using 10, 15 and 20 wt % solutions at 25 °C is 24%. Therefore, as a first step, the conversion is fixed at 20% and parameters were estimated at 25, 60 and 80 °C using 10, 15 and 20 wt% solutions. The parameter estimation is then extended to 50% conversion at 60 and 80 °C, as these temperatures could provide conversion greater than 50% for 10, 15 and 20 wt % solutions.

Figures 1–4 illustrates the estimated parameters as a function of temperature for 20% and 50% conversions. These values are with an interval at 95% confidence level. As seen in Figures 1–4, the confidence intervals are very close and/or overlap, implying reliable consistency of the estimated parameters. The average values (20 and 50% conversions) of α^* , β^* , ϵ_0 , and ϵ_1 are $0.776 \pm 0.11 \text{ s}^{-1} \text{ M}^{-1}$, $0.336 \pm 0.007 \text{ mol kJ}^{-1}$, $69.86 \pm 7.72 \text{ kJ mol}^{-1}$ and $-139.12 \pm 18.07 \text{ kJ mol}^{-1}$ respectively, over the range 25–80 °C and 10–20 wt% solutions. Since there is no other study reported on NaBH₄ self-hydrolysis kinetics based on the present approach, the comparison of the estimated values is not possible.

The estimated values of the apparent reaction order (m) as a function of temperature with an interval at 95% confidence level is illustrated in Figure 5 for 20 and 50% conversions. As seen, the apparent reaction order remains constant with extent of conversion at a particular temperature, while it decreases with temperature, irrespective of extent of conversion. The plausible explanation and/or interpretation for this observed effect is given in detail in the next section.

The comparison of experimental performance with model predicted performance using estimated parameters (Table 2) is carried out for all the experimental runs. The performance comparison at 60 °C for 20% and 50% conversion is illustrated in Figures 6–7. Similar trends are observed in all other cases

investigated. The good agreement between experimental performance and model predicted performance demonstrates that the estimated parameters can be used to satisfactorily correlate (or reproduce) the experimental kinetic data from which these parameters have been estimated. The rigorous statistical analysis of the estimated parameters (not given) using gPROMS showed that the values of the parameters estimated are statistically significant. The subsequent discussion delves further into possible physico-chemical interpretation of the estimated parameters.

5.2. Interpretation on the change in apparent reaction order with temperature

The apparent reaction order does not vary with extent of conversion at a particular temperature. However, it varies with temperature over the 0–50 % conversion range investigated (Figure 5). The order decreased from first-order to 0.26 with increase in temperature from 25 to 80 °C. The studies in highly diluted buffered NaBH₄ solutions (< 0.4 wt %, pH: 7.7–14) at low to medium temperatures (15–35 °C) and lower (< 5%) conversions reported first-order kinetics in NaBH₄ [18]. This is supported recently by Bartkus et al. [24], in a wide range of more concentrated solutions at medium temperature (0.5–25 wt% NaBH₄, 50 °C), which are non-buffered. However, the model was established in highly-base stabilized solutions so that pH remained approximately constant throughout the duration of the reaction. This is similar to pH controlled buffer solutions and may not hold true in the case of solutions where there is a significant change in solution pH during the progress of reaction.

Gonçalves et al. [20] obtained an order of 1.8 in NaBH₄ concentration over non-buffered, non-stabilized fairly concentrated solutions (10 wt%) at 45 °C. The value higher than unity reported in this study requires further analysis. Andreiux et al. [22] found a zero-order in NaBH₄ over 2.3–18.9 wt% solutions for 20 and 40 % conversions. This is the only study reported so far with respect to extent of conversion on NaBH₄ hydrolysis. The observed constant reaction order with extent of conversion is in good agreement with the present study. However, the estimation of reaction order is limited to one high temperature of 80 °C. There is also an uncertainty in the reported zero-order kinetics due to the poor R² values (0.66 and 0.61) as mentioned in section 1. These makes comparison difficult in terms of the value obtained and change in reaction order with temperature in the present study.

Churikov et al. [23] showed a first-order dependence in NaBH₄ concentration with their model applied to the experimental data of Andreiux et al. [22] on 18.9 wt% solution at 30 °C and approximately 25% conversions. This is in good agreement with the present study, where it was obtained first-order dependence in NaBH₄ concentration, in 10–20 wt% solutions at 25 °C and 0–20% conversions. The authors [23] also found that the first-order kinetics in NaBH₄ does not hold true in all their studied cases (0.5–7.2 wt% solution, 50–100 °C). The deviation from first-order kinetics might be due to the change in reaction temperature as observed in the present study. The experimental kinetic data used in the present study [39], as well as those reported by other authors [14, 22] on concentrated solutions at elevated temperatures, shows a deviation from first-order kinetics with increase in temperature. It is also worth noting that a variation in reactor order with temperature has been reported for complex epoxy-anhydride cure kinetics [40] and for oil shale pyrolysis [41].

In order to obtain an overall (or apparent) rate expression for the kinetics, the rates of chemical reactions must consider diffusion of reactants, intermediates, products and by-products [42]. The rates of diffusion of these species will depend on the physical state and viscosity of the solution through which they are diffusing and a change in these conditions will drastically affect the reaction kinetics [42]. The NaBH₄ self-hydrolysis as given by eq 1 is the complex reaction of solid NaBH₄ with liquid water, producing gaseous hydrogen and metaborate by-products, whose state (aqueous or solid) depends on the solution concentration. It is also well understood that the solution viscosity increases during the progress of self-hydrolysis reaction due to the formation of highly basic metaborate by-products. Most recently, Zhang et al. [43] observed a 2707% increase in solution viscosity at the completion of reaction at 25 °C using 20 wt% solution. This significant increase in solution viscosity can cause decrease in the rates of diffusion of species and might become the rate controlling step. This results in a decreased reaction rate during the progress of the reaction, i.e. with increase in reactant conversion.

The observed change in apparent reaction order during the progress of reaction might be explained as follows. The temperature has a significant effect on solution viscosity, which can be described in terms of Arrhenius-type relationships [44–46].

$$\eta = \eta_0 \exp\left(\frac{E_{af}}{RT}\right) \quad (16)$$

where η is the viscosity, η_0 the pre-exponential factor and E_{af} , the activation energy of flow. This implies that an increase in temperature decreases the solution viscosity. Viscosity is an indication of the solution resistance to flow and its reduction at high temperature enhances the interaction between reactant molecules. This in turn lessens the relative contribution of the effect of the concentration on the reaction rate. The observed deviation in the present study from first-order kinetics at low temperatures to fractional-order kinetics at higher temperatures can therefore be attributed to the decrease in solution viscosity.

5.3. Interpretation on the change in activation energy with NaBH₄ conversion

The activation energy and the pre-exponential factor, originally developed in homogeneous reaction kinetics, generally identify the energy barrier to the bond redistribution process during the transformation of well defined reactant(s) to identifiable product(s) for the rate determining step in a single reaction. The values therefore, must be constant and be characteristic of that particular chemical step or process [25–27]. Constant activation energy has been reported by various authors for the self-hydrolysis of NaBH₄ in highly diluted solutions (< 0.4 wt%) at low temperatures (15–35 °C) and for few initial percentages of NaBH₄ converted (< 5 wt%) [18]. This is justifiable since there will not be any significant change in solution properties under these conditions.

Andrieux et al. [22] reported constant activation energy of $98 \pm 10 \text{ kJ mol}^{-1}$ on non-stabilized, non-buffered, concentrated solution (18.9 wt%) at high temperatures (30–80 °C). Very similar value for activation energy is reported by Churikov et al. [23] on highly stabilized medium concentrated solutions (12–14.0 pH, 0.5–7 wt%) at high temperatures (50–100 °C). These models have limitation in terms of

constant reaction order approximation which leads to uncertainty in the reported values of the order of reaction, which in turn reflect in the estimated value of the activation energy. The dependence of activation energy (E_{ap}) with α computed by eq 8 using the estimated values of ε_0 , and ε_1 is shown in Figure 8. As seen, there is a variation in activation energy with NaBH_4 conversion, i.e. it increases from 65 ± 11 to $162 \pm 2 \text{ kJ mol}^{-1}$, with an increase in conversion from 0 to 50 %.

The change in activation energy with extent of conversion has been recognized for heterogeneous thermally stimulated reactions [25–27]. The variation in activation could be either an artifact resulting from numerical instability of the computational method, or a real variation that results from: (1) heterogeneous nature of the reaction that could cause changes in reaction kinetics during product formation, the physical state and structure of reactants and products, or other similar effects; (2) using a single-step kinetic assumption for a complex process involving multiple steps, each having unique activation energy; and (3) kinetic complexities resulting from heat and/or mass transfer at reaction interface, as well as from physical processes that have different activation energies, such as diffusion of a gaseous product, adsorption-desorption and sublimation, which have different activation energies. The variation of activation energy from all these effects gives an effective or apparent activation energy that varies with the extent of conversion. Hence the variation in activation energy could not be interpreted in terms of a free energy barrier [25–26, 31–32, 47]. However, the values of the apparent activation parameters (i.e. apparent activation energy and pre-exponential factor) enable one to model the process without an in-depth insight into its mechanism.

The error due to numerical instability occurs mainly in the differential method, where rates are computed from conversion-time curves. The present work employs a powerful numerical method, which may be expected to make negligible any possible error due to numerical instability. The recent study on NaBH_4 self-hydrolysis [22] on the characterization of hydrolysis intermediates shows that at conversions $< 22\%$, it is the direct reaction $\text{BH}_4^- \rightarrow \text{BH}_3(\text{OH})^-$ that occurs preferentially, and that at conversions $\geq 22\%$ the reaction is controlled by the formation of $\text{B}(\text{OH})_4^-$. Therefore, isoconversional methods assuming a single-step kinetic approximation may have some effect for the variation in activation energy. As discussed in the above section, NaBH_4 self-hydrolysis is a reaction between solid and liquid reactants producing gaseous hydrogen product and highly basic metaborate by-products, whose state (aqueous or solid) depends on the solution concentration. This causes a systematic change in solution properties in terms of pH and viscosity [18, 43] and might have a significant effect on the observed variation in activation energy with the extent of conversion.

The study on the influence of soluble solids content on viscosity by various authors [44–46] showed that the activation energy of flow (E_{af}) might increase or decrease depending on the type of soluble solids content. This effect can be described by the following expressions [44–46]:

$$\eta = \eta_1 C^{b_1} \quad (17)$$

$$\eta = \eta_2 \exp(b_2 C) \quad (18)$$

where η_i and b_i are constants and C is the concentration of the soluble solid content. Hence one may assume that the activation energy of flow increases with an increase in the extent of conversion due to rise in metabolate by-product formation, which in turn increases the activation energy of the self-hydrolysis reaction.

It is worth noting the influence of extent of conversion and initial NaBH_4 concentration on the rate of hydrolysis reaction in the model recently established by Bartkus et al. [24]. This is in line with the observation in the present study. Gawdzik et al. [48] attempted to include the impact of increase in viscosity in the kinetic model for the formation of linear living polymer and the model prediction is found to be nearer to the measurements. Incorporation of the change in solution viscosity in the present model would confirm its effect on self-hydrolysis kinetics. This would also expect to decouple the effect of change in solution viscosity resulted in the form of variation in activation energy, which in turn leads to constant value for activation energy.

A basic pH has been generally considered as the cause for reduced reaction rate and has been employed in prior kinetic studies [18, 20, 23–24]. A systematic analysis of the pH evolution from concentrated solutions at higher temperatures is carried out in the present study and found that it is not possible to explain the self-hydrolysis kinetics based on the observed changes in solution pH. On the other hand, it is possible to explain on the observed change in solution viscosity and is discussed below.

5.4. Interpretation on the change in pH on NaBH_4 self-hydrolysis kinetics

The prior kinetic studies in highly diluted (< 0.4 wt%) buffered (pH: 7.7–10.1) solutions, at low to medium temperature (15–35 °C) and lower conversions (< 5 wt%) showed a first-order dependence in hydrogen ion concentration [18]. Gonçalves et al. [20] reported an order of 1.2 on hydrogen ion concentration for non-buffered, non-stabilized, medium concentrated solutions (10 wt%) at medium to high temperatures (45–65 °C) for NaBH_4 self-hydrolysis. However, as mentioned in section 1, there is a mismatch between experimental and model predicted pH values, particularly during initial stage of the reaction, where the increase in pH is quite rapid and crucial in terms of H_2 production. Churikov et al. [23] observed an order of 1.8 for hydrogen ion concentration on highly diluted to medium concentrated (0.5–7 wt%) solutions, at medium to high temperatures (50–100 °C) which are highly base-stabilized (pH: 12–14). This is not in agreement with the earlier reported studies which demonstrated a decrease in apparent reaction order in hydrogen ion (to about 0.4) at higher values (12–14) of pH [18]. The recently established rate expression for hydrogen ion depletion by Bartkus et al. [24] is empirical in nature and does not allow, therefore gaining further theoretical insight on the influence of pH on the self-hydrolysis kinetics. Also, this model could not well predict the reaction at low values of solution pH. Thus, all these studies in spite of confirming the inhibition of self-hydrolysis reaction by basic pH, could not describe the influence of pH in a wide practical operating window.

With an objective of gaining more insight into the effect of pH on NaBH_4 self-hydrolysis kinetic mechanisms, the pH evolution during the course of reaction of 10–20 wt% solutions (non-buffered, non-stabilized), at 60 and 80 °C was systematically investigated. As far as the authors know, this is the first

study reporting pH evolution of NaBH₄ self-hydrolysis on concentrated solutions at higher temperatures. The effect of pH on initial NaBH₄ concentration is illustrated in Figure 9 (a-b). As seen, there is an increase in pH during the progress of hydrolysis reaction for all the studied NaBH₄ solutions irrespective of temperature, which is in agreement with the reported results [19–20, 22] for highly diluted to medium concentrated solutions at low to medium temperatures. It is important to note that, irrespective of temperature, higher values of pH are obtained for the lower initial NaBH₄ concentrations, i.e. 10 wt% solution having highest pH during the progress of reaction has got lowest reaction rate. This supports the generally accepted view on the influence of pH (inhibition of reaction rate) on NaBH₄ self-hydrolysis kinetics.

The effect of pH on NaBH₄ self-hydrolysis reaction temperature is illustrated in Figure 10 (a–c). As seen, irrespective of initial NaBH₄ concentrations, a higher value of pH is obtained at higher temperature throughout the progress of reaction. Reaction rate increases with temperature and this implies increase in pH with reaction rate. This is against the generally accepted influence of pH on NaBH₄ self-hydrolysis reaction kinetics where the rate is inhibited by pH. However, the observed increase in rate with increase in pH can be explained based on the change in solution viscosity. An increase in temperature reduces the solution viscosity, while enhancing the reaction rate by increasing the diffusion of reactant, intermediate and product molecules in the solution. This results in enhanced NaBH₄ conversion and/or formation of metabolite by-products, which in turn increases the solution pH.

The above explanation and/or interpretation holds true in the case of storage of NaBH₄ solutions by stabilizing it with a base and also with the acid-catalyzed hydrolysis of NaBH₄ solutions. Li et al. [49] demonstrated the sudden increase in viscosity of the NaBH₄ solutions with increase in pH by the addition of a base at various concentrations. Also, the continuous increase in temperature of the stabilized NaBH₄ solutions substantially promotes the self-hydrolysis reaction [14]. Kim et al. [50] using various organic acids found that not only the acidity (pH) but also the acid-type and chemical structure are important factor on hydrolysis of NaBH₄. Akdim et al. [51] showed that acetic acid, which has weaker acidity than HCl is as efficient as HCl for hydrogen generation from NaBH₄ using same acid–NaBH₄ ratio. It is worth mentioning that, for the same pH, higher reaction rate for acetic acid as opposed to hydrochloric acid has been reported for NaBH₄ self-hydrolysis [39]. This could be due to the differences in viscosity caused by these acids, i.e. for the same pH, a solution in acetic acid might exhibit lower viscosity than for hydrochloric acid.

6. Conclusions

The NaBH₄ self-hydrolysis kinetics is described by a model-based isoconversional method based on single-step kinetic approximation in a wide practical operating window of 10–20 wt% NaBH₄ solutions at 25–80 °C and 0–50% conversions. This approach has the potential to capture the change in reaction mechanism during the progress of reaction, as well as with temperature. The reaction mechanism is represented by a ‘reaction-order’ model. The apparent activation energy and pre-exponential factor are interrelated through the kinetic compensation effect (KCE). It was found that: (1) apparent reaction order

is independent of extent of conversion at constant temperature and varies with temperature irrespective of extent of conversion, i.e. it decreases from first-order to 0.26 with increase in temperature from 25 to 80 °C; (2) apparent activation energy is conversion dependent and varies with extent of conversion, i.e. it increases from 65 ± 11 to 162 ± 2 kJ mol⁻¹ with an increase in conversion from 0–50 %; and (3) there is a good agreement between model predicted and experimental performances.

Even though an increase in pH inhibits the self-hydrolysis reaction rate, the earlier studies could not well explain the influence of pH on self-hydrolysis kinetics of concentrated solutions at elevated temperatures, where, despite an increase in pH, the reaction rate is high. The change in reaction order with temperature and variation of activation energy during the progress of reaction implies the influence of solution viscosity on hydrolysis kinetics. The decrease in reaction order with temperature is due to the difference in interaction between reactant molecules due to reduced solution viscosity. It is possible that the variation of the apparent activation energy with extent of conversion is associated with change in activation energy of flow due to variation in soluble solid contents during the progress of reaction in terms of depletion of NaBH₄ and formation of metaborate by-products.

The present work enables modeling of the self-hydrolysis process without much deeper insight into its mechanism. Better focused experimental and modeling studies to include the impact of increase in solution viscosity during the progress of the self-hydrolysis reaction is instrumental for the deeper insight into its mechanism.

Acknowledgement

Support for research partnership between National Laboratory of Energy and Geology, Portugal and University of South Carolina, USA was provided by Luso-American Foundation, in collaboration with National Science Foundation via the “2010 PORTUGAL - U.S. Research Networks Program”.

5. References

- [1] 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 Ame Chem Soc* 1953;75:215-219.
- [2] Marrero-Alfonso EY, Gray JR, Davis TA, Matthews MA. Minimizing water utilization in hydrolysis of sodium borohydride: The role of sodium metaborate hydrates. *Int J Hydrogen Energy* 2007;32:4723-4730.
- [3] Cavaliere S, Hannauer J, Demirci, UB, Akdim O, Miele P. Ex situ characterization of N₂H₄, NaBH₄, and NH₃BH₃, reduced cobalt catalysts in NaBH₄ hydrolysis. *Catal. Today* 2011;170: 3-12.
- [4] Kojima Y, Kawai Y, Nakanishi H, Matsumoto S. Compressed hydrogen generation using chemical hydride. *J Power Sources* 2004;135:36-41.
- [5] Demirci UB, Garin F. Promoted sulphated-zirconia catalysed hydrolysis of sodium tetrahydroborate. *Catal Commun* 2008;9:1167-1172.

- [6] Amendola SC, Sharp-Goldman SL, Janjua MS, Kelly MT, Petillo PJ, Binder M. An ultrasafe hydrogen gas generator: Aqueous, alkaline borohydride solutions and Ru Catalyst. *J Power Sources* 2000;85:186-189.
- [7] Amendola SC, Sharp-Goldman SL, Janjua MS, Spencer NC, Kelly MT, Petillo PJ, Binder M. A safe, Portable, Hydrogen gas generator using aqueous borohydride solution and Ru Catalyst. *Int J Hydrogen Energy* 2000;25:969-975.
- [8] Demirci UB, Akdim O, Miele P. Ten-year efforts and a no-go recommendation for sodium borohydride for on-board automotive hydrogen storage. *Int. J. Hydrogen Energy* 2009;34:2638-2645.
- [9] Demirci UB, Akdim O, Andrieux J, Hannauer J, Chamoun R, Miele, P. Sodium borohydride hydrolysis as hydrogen generator: Issues, state of the art and applicability upstream from a fuel cell. *Fuel Cells* 2010;10:335-350.
- [10] Minkina VG, Shabunya SI, Kalinin VI, Martynenko VV, Smirnova AL. Long-term stability of sodium borohydride for hydrogen generation. *Int. J. Hydrogen Energy* 2008;33:5629-5635.
- [11] Minkina VG, Shabunya SI, Kalinin VI, Martynenko VV. Stability of aqueous-alkaline sodium borohydride formulations. *Russ. J. Applied Chemistry* 2008;81:380-385.
- [12] Minkina VG, Shabunya SI, Kalinin VI, Martynenko VV, Smirnova AL. Stability of alkaline aqueous solutions of sodium borohydride. *Int. J. Hydrogen Energy* 2012;37:3313-3318.
- [13] Shabunya SI, Minkina VG, Nesteruk AA, Martynenko VV, Kalinin VI. Experimental studies of the hydrolysis kinetics of aqueous-alkaline solutions of sodium borohydride. *Russ. J. Applied Chemistry* 2012;85:1167-1175.
- [14] Moon GU, Lee SS, Lee KY, Kim SH, Song KH. Behavior of hydrogen evolution of aqueous sodium borohydride solutions. *J Ind Engg Chem* 2008;14:94-99.
- [15] Aiello R, Sharp JH, Matthews MA. Production of hydrogen from chemical hydrolysis via hydrolysis with steam. *Int. J. Hydrogen Energy* 1999;24:1123-1130.
- [16] Beaird AM, Davis TA, Matthews MA. Deliquescence in the hydrolysis of sodium borohydride by water vapor. *Ind. Eng. Chem. Res.* 2010;49:9596-9599.
- [17] Liu H, Boyd CM, Beaird AM, Matthews MA. Vapor phase batch hydrolysis of NaBH_4 at elevated temperatures and pressure. *Int. J. Hydrogen Energy* 2011;36:6472-6477.
- [18] Retnamma R, Novais AQ, Rangel CM. Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: A review. *Int. J. Hydrogen Energy* 2011;36: 9772-9790 and references therein.
- [19] Gonçalves A, Castro P, Novais AQ, Fernandes VR, Rangel CM, Matos M. Dynamic modeling of hydrogen generation via hydrolysis of sodium borohydride, *Chem Engg Trans* 2007;12:243-248 Editor: Jiri Klemes, AIDIC, Italy.
- [20] Gonçalves A, Castro P, Novais A, Rangel CM, Matos M. Modeling of catalytic hydrogen generation from sodium borohydride, *Computer Aided Chemical Engg* 2008; 25:757. Editors: Bertrand Braunschweig and Xavier Joulia, Elsevier.
- [21] Davis RE, Bromels E, Kibby CL. Borohydrides III. Hydrolysis of sodium borohydride in aqueous

- solution. *J. Am. Chem. Soc.* 1962;84:885-889.
- [22] Andrieux J, Demirci UB, Hannauer J, Gervais C, Goutaudier C, Miele P. Spontaneous hydrolysis of sodium borohydride in harsh conditions. *Int. J. Hydrogen Energy* 2011;36:224-233.
- [23] Churikov AV, Gamayunova IM, Zapsis KV, Churikov MA, Ivanishchev AV. Influence of temperature and alkalinity on the hydrolysis rate of borohydride ions in aqueous solution. *Int. J. Hydrogen Energy* 2012;37:335-344.
- [24] Bartkus TP, Tien JS, Sung C-J, A semi-global reaction rate model based on experimental data for the self-hydrolysis kinetics of aqueous sodium borohydride. *Int. J. Hydrogen Energy* 2013;38:4024-4033.
- [25] Vyazovkin S. Kinetic concepts about thermally stimulated reactions in solids: A view from a historical perspective. *Int. Rev. Phys. Chem.* 2000;19:45-60.
- [26] Galway AK. What can we learn about the mechanisms of thermal decomposition of solids from kinetic measurements?. *J. Therm. Anal. Calorimetry* 2008;92:967-983.
- [27] Vyazovkin S, Burnham AK, Criado JM, Perez-Maqueda AA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics committee recommendations for performing kinetic computations on thermal analysis data. *Therm. Chim. Acta* 2011;520:1-9.
- [28] Simon P. Isoconversional methods: Fundamentals, meaning and application. *J. Therm. Anal. Calorimetry* 2004;76:123-132.
- [29] Simon P. The single-step approximation: Attributes, strong and weak sides. *J. Therm. Anal. Calorimetry* 2007;88:709-715.
- [30] Khawam A, Flanagan DR. Role of isoconversional methods in varying activation energies of solid-state kinetics I. isothermal kinetic studies. *Therm. Chim. Acta* 2005;429:93-102.
- [31] Galway AK. What is meant by the term 'variable activation energy' when applied in the kinetic analyses of solid state decompositions (crystolysis reactions)?. *Therm. Chim. Acta* 2003;397: 249-268.
- [32] Vyazovkin S. Reply to "What is meant by the term 'variable activation energy' when applied in the kinetic analyses of solid state decompositions (crystolysis reactions)?. *Therm. Chim. Acta* 2003;397:269-271.
- [33] Brudrugaec P, Segal E. On the apparent compensation effect found for two consecutive reactions. *J. Therm. Anal. Calorimetry* 2000;62:227-235.
- [34] Brudrugaec P, Popescu C, Segal E. Change of the apparent reaction order with temperature as a consequence of the reaction mechanism complexity. *J. Therm. Anal. Calorimetry* 2001;64:821-827.
- [35] Lesnikovich AI, Levchik SV. A method of finding invariant values of kinetic parameters. *J. Therm. Anal.* 1983;27:89-94.
- [36] Brudrugaec P, Segal E. On the compensation effect at the form of the differential conversion function. *J. Therm. Anal. Calorimetry* 1998;53:269-283.
- [37] Brown MW, Galway AK. The significance of "compensation effects" appearing in data published in "Computational Aspects of Kinetic Analysis": ICTAC project, 2000. *Therm Chim Acta.* 2002;387:173-183.

- [38] Budrugaec P, Homentcovschi D, Segal E. Critical analysis of the isoconversional methods for evaluating the activation energy I. Theoretical background. *J. Therm. Anal. Calorimetry* 2001;63: 457-463.
- [39] Yu Lin, Matthews MA. Hydrolysis of sodium borohydride in concentrated aqueous solution. *Int. J. Hydrogen Energy* 2011;36:7416-7422.
- [40] Vyazovkin S, Sbirrazzuoli N. Kinetic methods to study isothermal and nonisothermal epoxy-anhydride cure. *Macromol. Chem. Phys.* 1991;2000:2294-2303.
- [41] AL-Ayed OS. Variable reaction order for kinetic modeling of oil shale pyrolysis. *Oil Shale* 2011; 28:296-308.
- [42] Flynn JH. A critique of lifetime prediction of polymers by thermal analysis. *J. Therm. Anal.* 1995; 44:499-512.
- [43] Zhang X, Wei Z, Guo Q, Tian H. Kinetics of sodium borohydride hydrolysis catalyzed via carbon nanosheets supported Zr/Co. *J Power Sources* 2013;231:190-196.
- [44] Ibarz A, Gonzalez C, Esplugas S, Vicente M. Rheology of clarified fruit juices. I: Peach juices. *J. Food Eng.* 1992;15:49-61.
- [45] Ibarz A, Pagan J, Miguelsanz R. Rheology of clarified fruit juices. II: Blackcurrant juices. *J. Food Eng.* 1992;15:63-73.
- [46] Ibarz A, Garvin A, Costa J. Rheological behavior of sloe (*prunus spinosa*) fruit juices. *J Food Eng.* 1996;27:423-430.
- [47] Vyazovkin S. Two types of uncertainty in the values of activation energy. *J. Therm. Anal. Calorimetry* 2001;64:829-835.
- [48] Gawdzik A, Mederska A, Mederski T. Effect of viscosity change of reaction mixture on the kinetics of formation of linear living polymer. *Ecol Chem Eng A* 2012;19(11):1393-1403.
- [49] Li ZP.; Liu BH, Arai K, Asaba K, Suda S. Evaluation of alkaline borohydride solutions as the fuel for fuel cell. *J. Power Sources* 2004;126:28-33.
- [50] Kim HJ, Shin KY, Kim HJ, Han MK, Kim H, Shul YG, Junj KT. Hydrogen generation from aqueous acid-catalyzed hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* 2010;35:12239-12245.
- [51] Akdim O, Demirci UB, Miele P. Acetic acid, a relatively green single-use catalyst for hydrogen generation from sodium borohydride. *Int. J. Hydrogen Energy* 2009;34:7231-7238.

List of Tables

Table 1. Details of hydrolysis experiments.

Table 2. Estimated parameters for 0-50% conversions.

Table 1. Details of hydrolysis experiments.

T (°C)	NaBH ₄ (wt %)	Duration (hr)	Final NaBH ₄ conversion (%)
25	10	23.0	30
	15	24.0	27
	20	24.0	24
60	10	25.0	92
	15	23.5	75
	20	23.5	62
80	10	13.5	88
	15	24.0	98
	20	24.0	98

Table 2. Estimated parameters for 0-50% conversions.

Parameter	20 %	50%	0-50% (Mean)
α^* ($s^{-1} M^{1-m}$)	0.774±0.088	0.777±0.132	0.776±0.110
β^* ($mol\ kJ^{-1}$)	0.335±0.003	0.336±0.011	0.336±0.007
ε_0 ($kJ\ mol^{-1}$)	68.276±8.57	70.435±6.87	69.86±7.72
ε_1 ($kJ\ mol^{-1}$)	-139.39±20.84	-140.12±15.29	-139.76±18.07
m (25 °C)	0.975±0.074	-	0.975±0.074
m (60 °C)	0.456±0.013	0.433±0.027	0.444±0.020
m (80 °C)	0.284±0.006	0.238±0.051	0.261±0.029

List of Figures

Figure 1. Plots of α^* as a function of temperature for 20% and 50% conversions.

Figure 2. Plots of β^* as a function of temperature for 20% and 50% conversions.

Figure 3. Plots of ε_0 as a function of temperature for 20% and 50% conversions.

Figure 4. Plots of ε_1 as a function of temperature for 20% and 50% conversions.

Figure 5. Change in reaction order (m) with temperature and conversion.

Figure 6. Comparison of model predictions with measurements for 20% conversion at 60 °C: (a) 10 wt% solution; (b) 15 wt% solution; (c) 20 wt% solution; markers: measured values; solid line: predicted values.

Figure 7. Comparison of model predictions with measurements for 50% conversion at 60 °C: (a) 10 wt% solution; (b) 15 wt% solution; (c) 20 wt% solution; markers: measured values; solid line: predicted values.

Figure 8. Change in activation energy with conversion.

Figure 9. Effects of pH on initial borohydride concentrations: (a) 60 °C; (b) 80 °C

Figure 10. Effects of pH on temperature: (a) 10 wt% solutions; (b) 15 wt% solutions; (c) 20 wt% solutions.

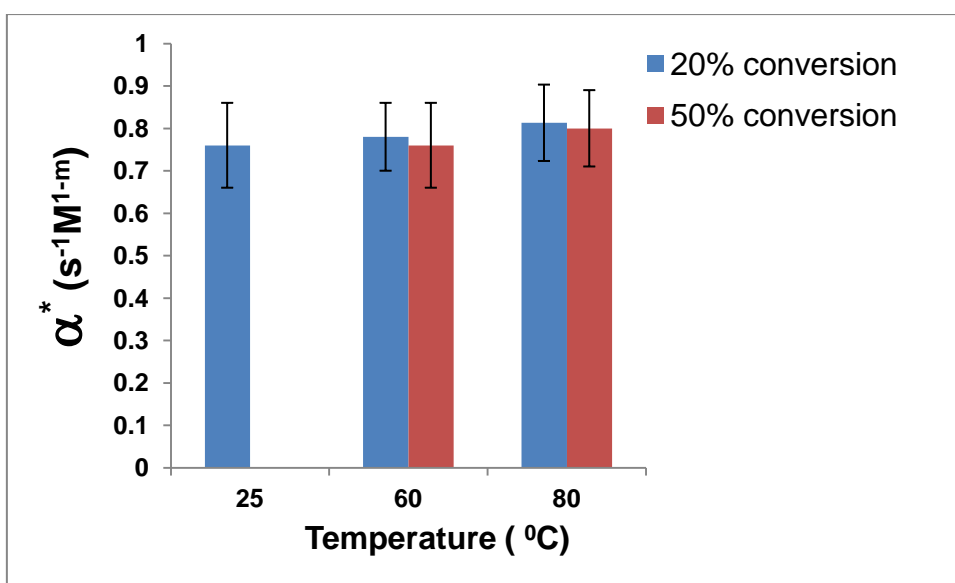


Figure 1. Plots of α^* as a function of temperature for 20% and 50% conversions.

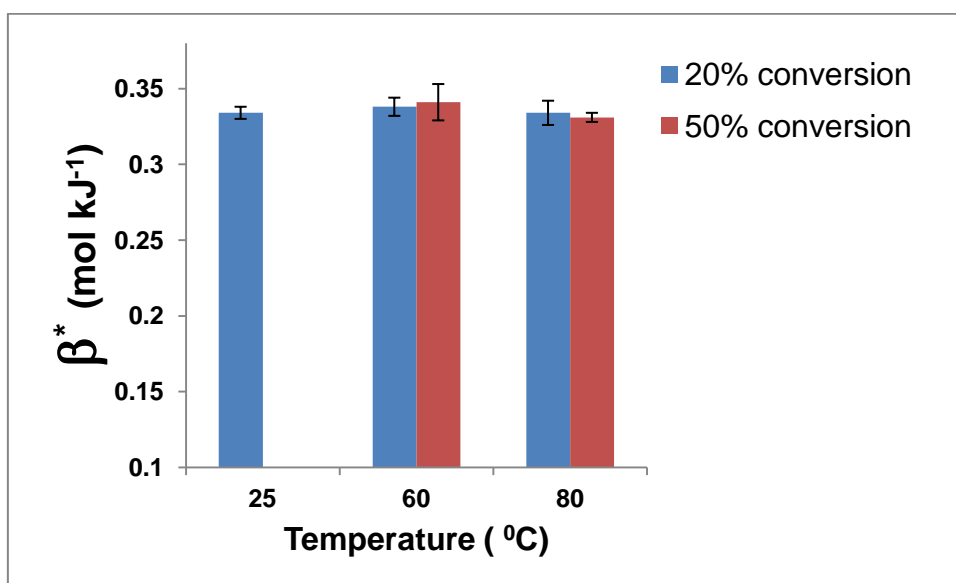


Figure 2. Plots of β^* as a function of temperature for 20% and 50% conversions.

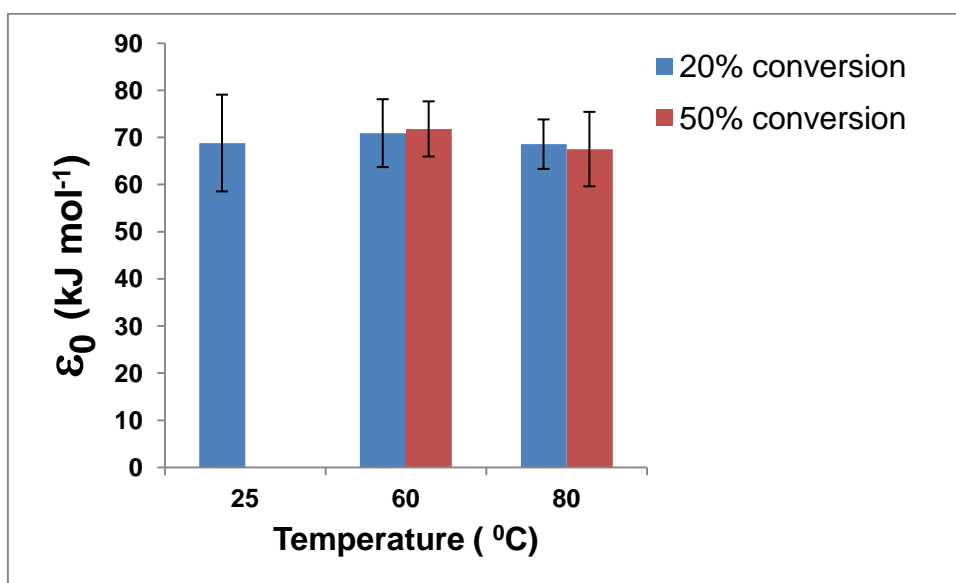


Figure 3. Plots of ϵ_0 as a function of temperature for 20% and 50% conversions.

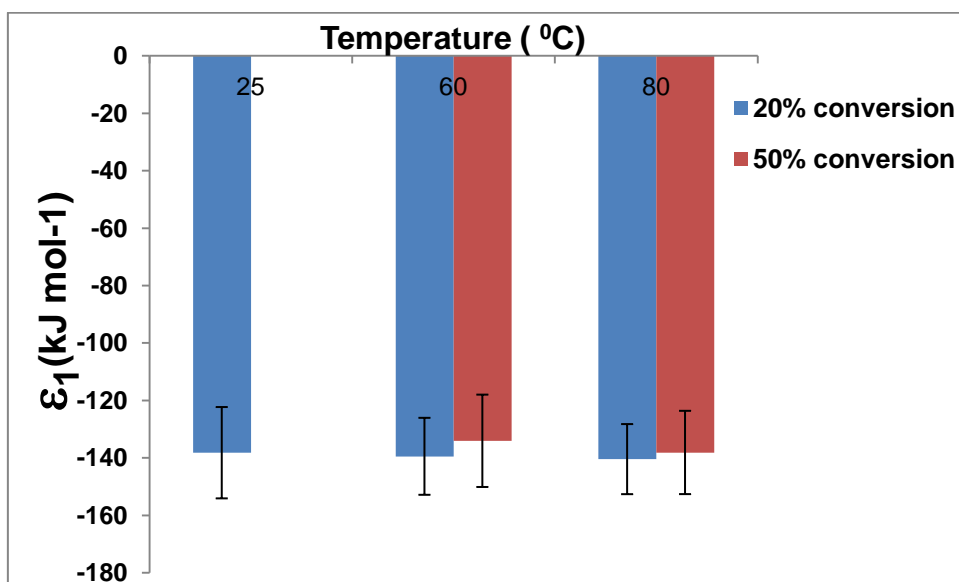


Figure 4. Plots of ϵ_1 as a function of temperature for 20% and 50% conversions.

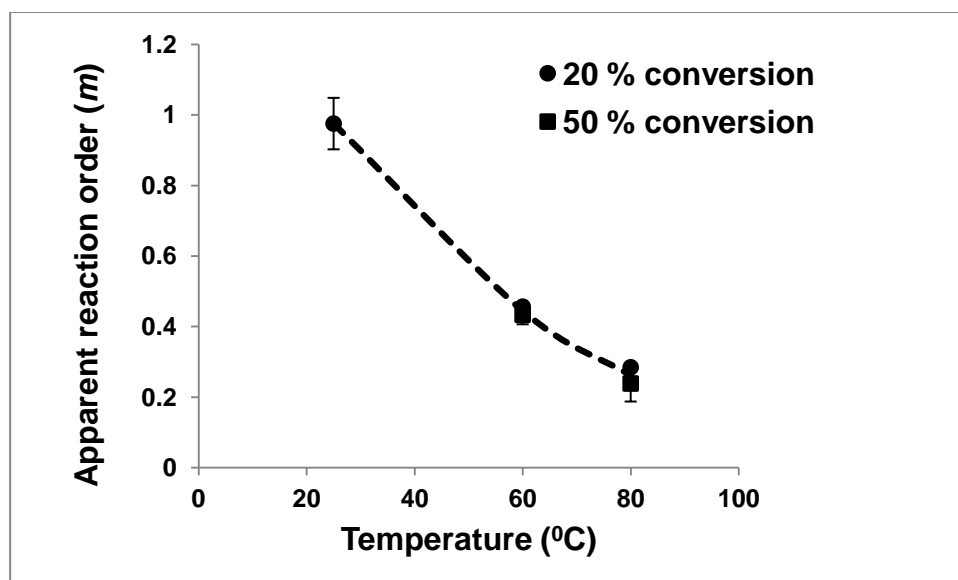


Figure 5. Change in reaction order (m) with temperature and conversion.

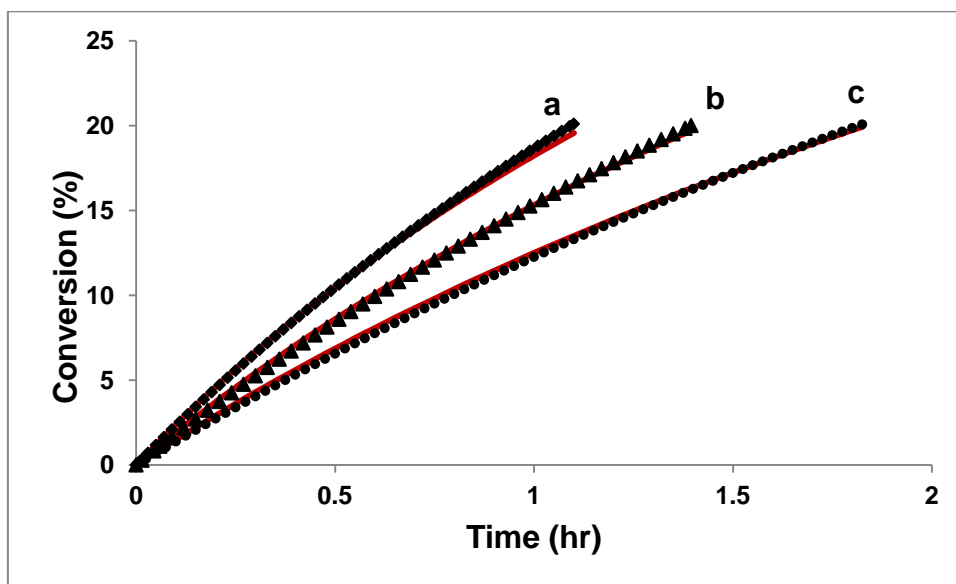


Figure 6. Comparison of model predictions with measurements for 20% conversion at 60 °C: (a) 10 wt% solution; (b) 15 wt% solution; (c) 20 wt% solution; markers - measured values; solid line: predicted values.

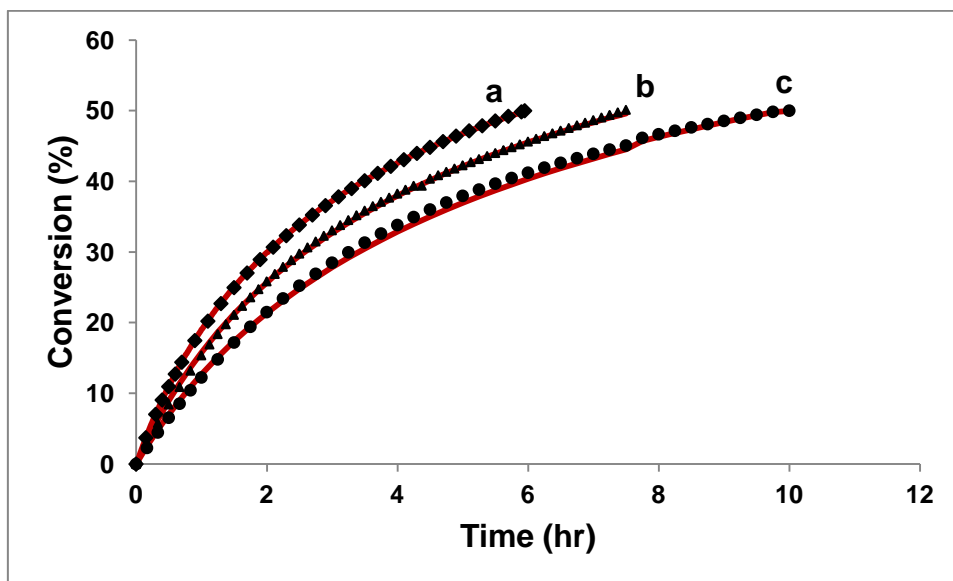


Figure 7. Comparison of model predictions with measurements for 50% conversion at 60 °C: (a) 10 wt% solution; (b) 15 wt% solution; (c) 20 wt% solution; markers - measured values; solid line: predicted values

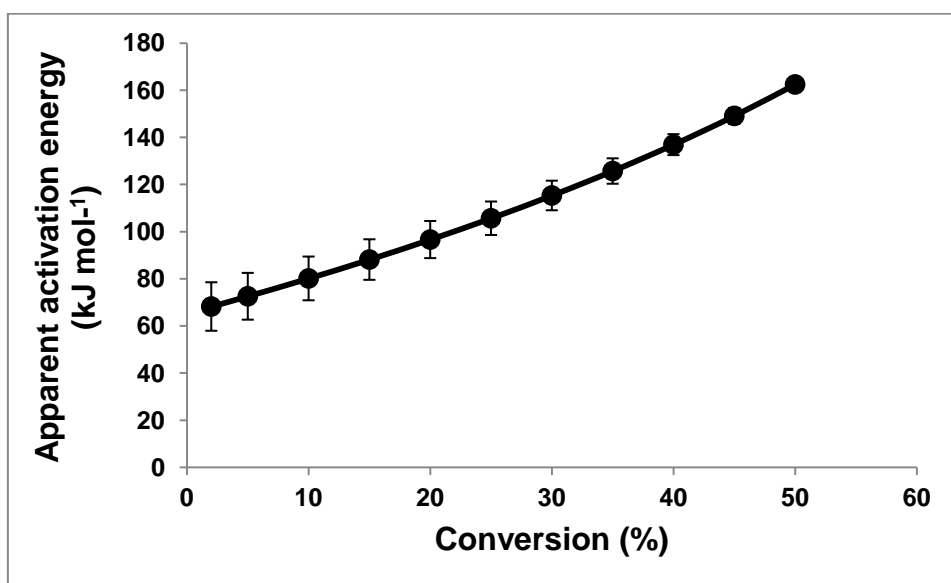


Figure 8. Change in activation energy with conversion.

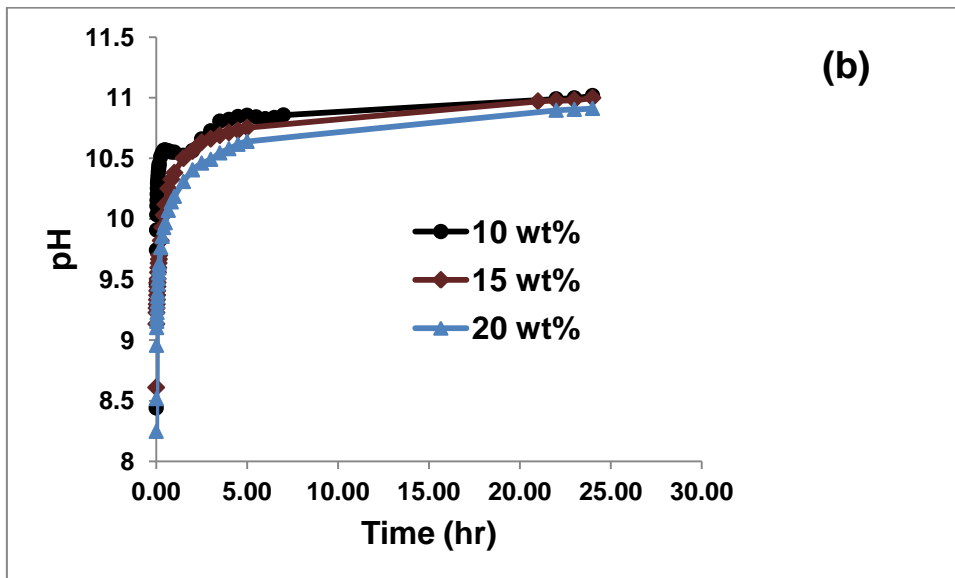
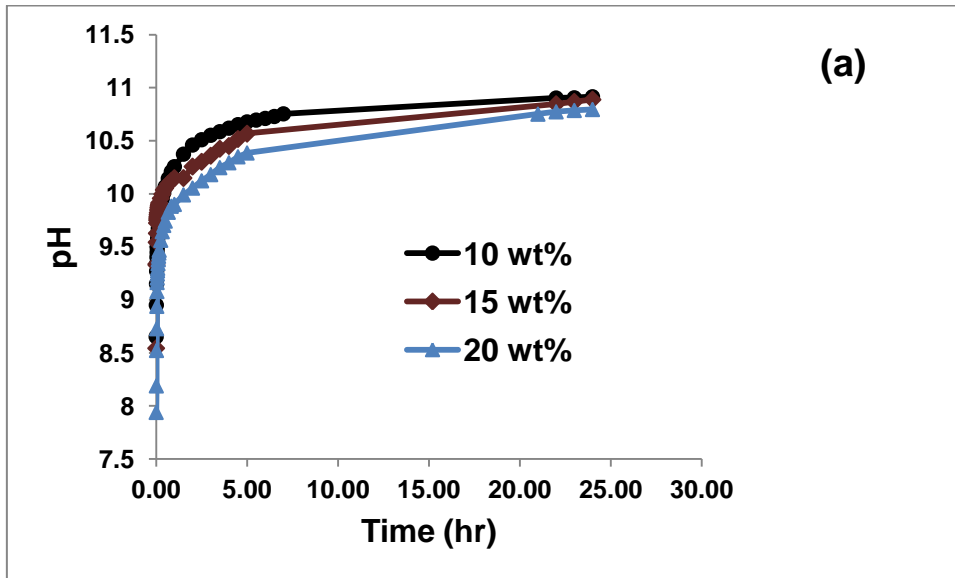


Figure 9. Effects of pH on initial borohydride concentrations: (a) 60 °C; (b) 80 °C

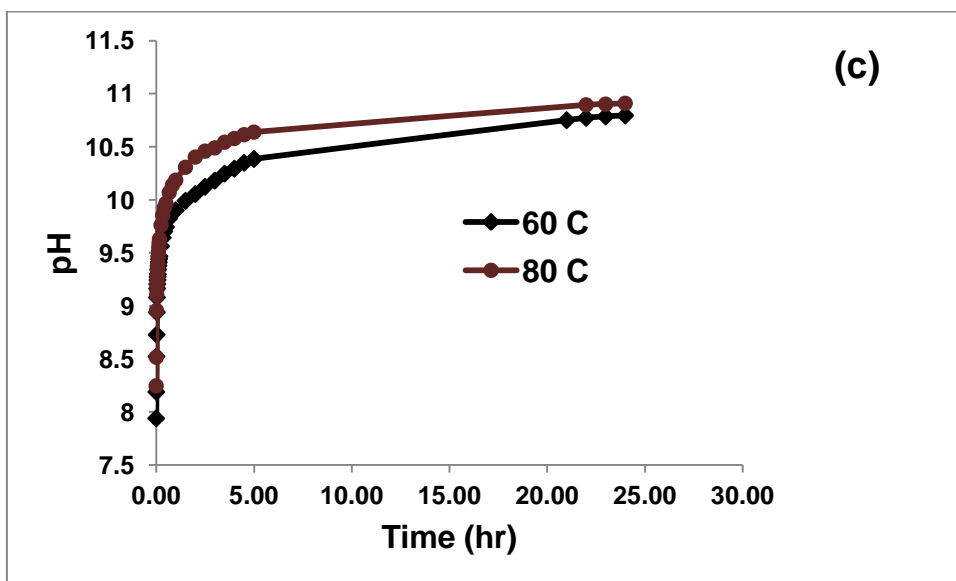
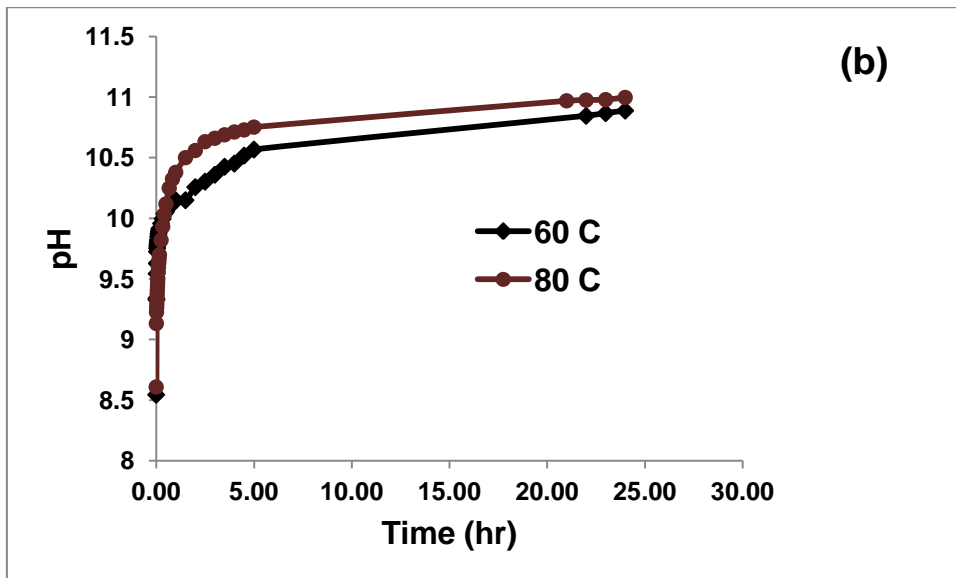
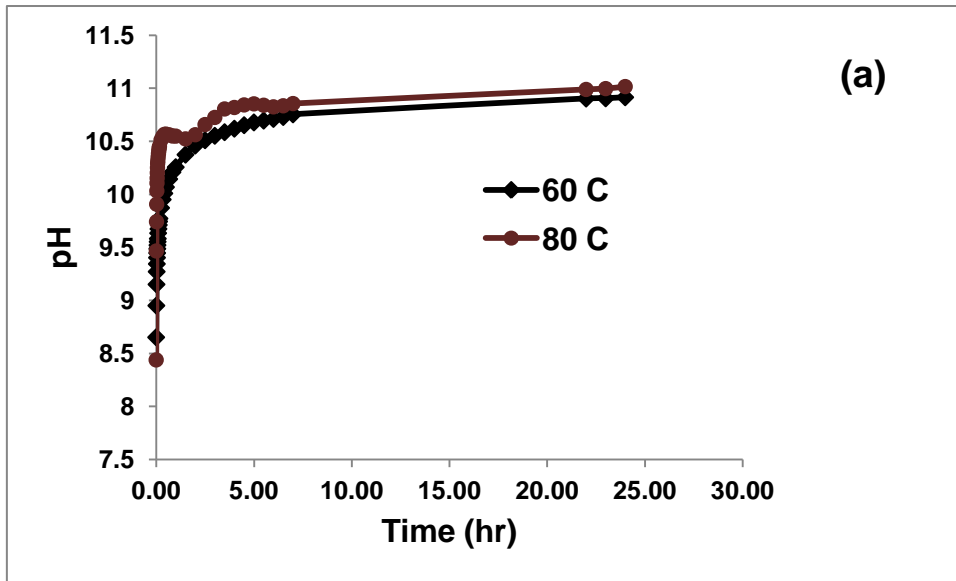


Figure 10. Effects of pH on temperature: (a) 10 wt% solutions; (b) 15 wt% solutions; (c) 20 wt% solutions.

Referees

1. Umit B. Demirci

Institut Européen des Membranes
Université Montpellier 2, CNRS, UMR 5253
Laboratoire des Agrégats Interfaces et Matériaux pour l'Energie
Place Eugène Bataillon
34095 Montpellier Cedex 5, France
E-mail: umit.demirci@iemm.univ-montp2.fr

2. D.M.F. Santos

Materials Electrochemistry Group
Instituto Superior Técnico
TU Lisbon, Av. Rovisco Pais
1049-001 Lisboa, Portugal
E-mail: diogosantos@ist.utl.pt

3. Pier Paolo Prosini

ENEA IDROCOMB, Italian National Agency for New Technologies
Energy and Sustainable Economic Development
C.R. Casaccia, Santa Maria di Galeria, Rome 00123, Italy
E-mail: pierpaolo.prosini@enea.it

4. Rui Chen

Department of Aeronautic and Automotive Engineering
Loughborough University
Loughborough, Leicestershire LE11 3TU, UK.
E-mail: r.chen@lboro.ac.uk

5. Saim Ozkar

Department of Chemistry
Middle East Technical University
06531 Ankara, Turkey
E-mail: sozkar@metu.edu.tr

6. Zhou-Peng Li

Department of Chemical and Biological Engineering

Zhejiang University

Hangzhou 310027, P.R. China,

E-mail: zhoupengli@zju.edu.cn