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Thermodynamic Study on the Solubility of NaBH4 and NaBO2 in NaOH Solutions

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Abstract

Extensive research has been performed for on-board hydrogen generation, such as pyrolysis of metal hydrides (e.g. LiH, MgH2), hydrogen storages in adsorption materials (e.g. carbon nanotubes and graphites), compressed hydrogen tanks and the hydrolysis of chemical hydrides. Among these methods, the hydrolysis of NaBH4 has attracted great attention due to the high stability of its alkaline solution and the relatively high energy density, with further advantages such as moderate temperature range (from –5oC to 100oC) requirement, non-flammable, no side reactions or other volatile products, high purity H2 output. The H2 energy density contained by the system is fully depend on the solubility of the complicated solution contains reactant, product and the solution stabiliser. In this work, an approach based on thermodynamic equilibrium was proposed to model the relationship between the solubility of an electrolyte and temperature, and the effect of another component on its solubility. The relationship was then applied to NaBH4 and NaBO2 aqueous solutions, and the effect of introduction of NaOH on their solubility after deriving their solubility from phase diagrams. The data has been shown in good agreement with the proposed model.

Key words

Sodium Borohydride, Hydrogen Production, Hydrogen Storage, Solubility, Hydrolysis

1. Introduction

With the increasing concern about air pollution and oil depletion, hydrogen, H_2, has been intensively studied as an alternative energy source. The main problem with hydrogen application is that it is not readily transported in bulk. In order to use hydrogen widely, especially for mobile applications, a compact and safe method for storage is needed. Various methods have been developed for H_2 storage, such as high-pressure gas [1], liquefied hydrogen [2, 3], adsorption on materials with high specific surface area [4], reforming of natural gas, alcohols and hydrocarbons[5, 6], catalytic reduction of water with metals [7], and slush hydrogen [8] etc. Each of these technologies has its inherited advantages as well as drawbacks, but the still poor stored energy density remains. One alternative solution which has potential to store more H_2 safely for mobile applications is to utilize the catalytic reduction of water with hydrides [9-11]. There are many different types of hydrides which has the potential to react with water and produce hydrogen gas. To use such materials for H_2 production for mobile applications, the energy density and the system operation safety are the major concerns. Table 1 listed the energy release during the hydrolysis reaction from a number of typical hydrides. It can be seen that most reactions between metal hydrides and water are vigorous. The large amount of heat can be released during the reaction which may cause explosion. Table 2 listed the density of these potential hydrides. Apart from LiH which clearly shows the safety concern, the sodium borohydride, $NaBH_4$, has the least weight density. In comparison, it is clear that $NaBH_4$ produces the least heat energy during the hydrolysis reaction while has a low weight density. It has therefore the potential to be a successful candidate as an alternative hydrogen storage technology for mobile application in particular.

Table 1 Heat released for 1gram hydrogen with different hydrides [12]

Hydrides	$NaBH_4$	LiH	$LiAlH_4$	$NaAlH_4$	CaH_2
$\Delta H°(kJmol^{-1})$	-27.1	-54.3	-62.5	-56.2	-58.0

Table 2 Weight of reductants necessary for 1 gram of hydrogen

Hydrides	$NaBH_4$	LiH	$LiAlH_4$	$NaAlH_4$	CaH_2
Weight(g)	4.73	4.00	12.2	14.3	10.5

The generation of hydrogen from $NaBH_4$ in aqueous solution is shown in Eq.(1). It can be seen that one mole of $NaBH_4$ in a water solution reacts with 2 moles of the water and produces 4 moles of H_2 and one mole of sodium metaborate ($NaBO_2$) as a by-product. Half of the produced H_2 is extracted from the water.

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \tag{1}$$

As a by-product, $NaBO_2$ has to be removed during the hydrolysis reaction to avoid clogging the catalyst which will significantly reduce the system reaction efficiency [13, 14]. A practical way to remove the $NaBO_2$ from the catalytic reaction bed is to dissolve it into the water left from the hydrolysis reaction and bring the solution into a exhaust system. Clearly, the water contained in the $NaBH_4$ hydrolysis reaction system has to not only cover the hydrolysis reaction but also to dissolve and remove the by-product. Too much water will reduce the hydrogen generation density of the system [15, 16], while insufficient water may results in catalyst clogging and reduce the system reaction efficiency. This necessitates the optimisation of the $NaBH_4$ concentration. In order to identify the optimised concentration, a semi-empirical simulation method based on dissolution equilibrium principles has been developed and reported in this paper

2. Theoretical Solubility Model

When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated, i.e. an equilibrium between undissolved and dissolved solutes is reached. This dissolution equilibrium can be expressed in a general term:

$$\mathrm{AB}\cdot n\mathrm{H_2O} \xleftrightarrow{K} \mathrm{A}^{+} + \mathrm{B}^{-} + n\mathrm{H_2O} \tag{2a}$$

where n is number of water crystallized with the solute AB, and K is the equilibrium constant.

Due to the interaction among the dissolved substances and the solvent, the performances of the dissolved substances in a real solution differ from that in the ideal-dilute one. Such differences are represented by the activities of the substances in the solution. Hence, the equilibrium constant of the dissolution can be expressed as

$$K = \frac{a_{\mathrm{A}^+} a_{\mathrm{B}^-} {a_{\mathrm{H_2O}}}^{n}}{a_{\mathrm{AB\cdot nH_2O}}} \tag{2b}$$

where a_i is the activity, and the subscript i denotes the substances.

Activity coefficient of a substance is defined as the ratio between activity and ideal-dilute concentration,

$$\gamma_i = \frac{a_i}{m_i / m_i^0} \tag{3}$$

where m_i is the molarity of substance i in the solution, which is the moles of substance contained by 1000g of solvent in the solution, and m_i^0 is the molarity of the substance at standard conditions.

The activity of a solid material is unity. Since the water is the bulk phase in the solution, its activity is assumed to be a constant. Substitute Eq.(3) into (2b), the equilibrium constant can then be obtained as

$$K = {a_{\mathrm{H_2O}}}^{n} \gamma_{\mathrm{A}^+} \gamma_{\mathrm{B}^-} m_{\mathrm{A}^+} m_{\mathrm{B}^-} = K_\gamma m_{\mathrm{A}^+} m_{\mathrm{B}^-} \tag{4}$$

If the molarity of substance A^+ equal to that of B^- and the solute AB in the solution, $m_{A^+} = m_{B^-} = m_{AB}$ then the equilibrium constant Eq.(4) can be further simplified as

$$K = K_\gamma m_{\mathrm{AB}}{}^2 \tag{5}$$

The equilibrium constant changes with temperature. This can be expressed using the van't Hoff equation [17]

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \text{ or } \frac{d\ln K}{d(1/T)} = \frac{\Delta H^\circ}{R} \tag{6}$$

where T is temperature, $\Delta H°$ is the change of enthalpy of the dissolution process which equals to the molar heat of solution and R is the universal gas constant.

Integration of the van't Hoff equation and substitute the equilibrium constant with Eq.(6), gives

$$2\ln m_{\mathrm{AB}} = -\frac{\Delta H^\circ_{\mathrm{AB}}}{RT} + C \tag{7}$$

where C is an integration constant, which includes all the activity coefficients.

Rearrange Eq.(7) then gives the molality of the solute AB in the saturated solution,

$$m_{\mathrm{AB}} = Ae^{-\Delta H^0_{\mathrm{AB}}/2RT} \tag{8}$$

For sodium borohydride, $NaBH_4$, two potential crystalline states, $NaBH_4 \cdot 2H_2O$ and $NaBH_4$, may exist as the undissolved solid in its saturated solution depending upon the temperature of the solution as shown in Eq.(9a,b) [18]. When the temperature is lower than 309.4K, the undissolved part is in the form of $NaBH_4 \cdot 2H_2O$. Above this temperature, the undissolved part is in the form of pure $NaBH_4$.

$$\mathrm{NaBH_4 \cdot 2H_2O} \xleftrightarrow{K_1} \mathrm{Na^+ + BH_4^- + 2H_2O} \quad (\mathrm{T < 309.4K}) \tag{9a}$$

$$\mathrm{NaBH_4} \xleftrightarrow{K_2} \mathrm{Na^+ + BH_4^-} \quad (\mathrm{T > 309.4K}) \tag{9b}$$

For sodium metaborate, $NaBO_2$, there are three crystalline states in the saturated sodium metaborate solution $NaBO_2 \cdot 4H_2O$, $NaBO_2 \cdot 2H_2O$, and $NaBO_2 \cdot 1/2H_2O$, as shown in Eq.(10a,b,c). Again, the solubility of each states depends on the temperature of the solution [19].

$$\mathrm{NaBO_2 \cdot 4H_2O} \longleftrightarrow \mathrm{Na^+ + B(OH)_4^- + 2H_2O} \quad (273 < \mathrm{T} < 326.6\mathrm{K}) \tag{10a}$$

$$\mathrm{NaBO_2 \cdot 2H_2O} \longleftrightarrow \mathrm{Na^+ + B(OH)_4^-} \quad (326.6 < \mathrm{T} < 378\mathrm{K}) \tag{10b}$$

$$\mathrm{NaBO_2 \cdot 1/2H_2O + 3/2H_2O} \longleftrightarrow \mathrm{Na^+ + B(OH)_4^-} \quad (\mathrm{T > 378K}) \tag{10c}$$

Using Eq.(7) and (8), the solubility of both $NaBH_4$ and $NaBO_2$ in terms of molality can be obtained as

$$2\ln m_{\mathrm{NaBH_4}} = -\frac{\Delta H^{\circ}_{\mathrm{NaBH_4}}}{RT} + C \tag{11}$$

$$2\ln m_{\mathrm{NaBO_2}} = -\frac{\Delta H^{\circ}_{\mathrm{NaBO_2}}}{RT} + C \tag{12}$$

which gives

$$m_{\mathrm{NaBH_4}} = Ae^{-\Delta H^{0}_{\mathrm{NaBH_4}}/2RT} \tag{13}$$

$$m_{\mathrm{NaBO_2}} = A'e^{-\Delta H^{0}_{\mathrm{NaBO_2}}/2RT} \tag{14}$$

where, $\Delta H^{\circ}_{\mathrm{NaBH_4}}$ and $\Delta H^{\circ}_{\mathrm{NaBO_2}}$ is the standard enthalpy change of sodium metaborate solution, which equals to the molar heat of solution. C is an integral constant, which is related to the overall activity coefficient, and R is the universal gas constant.

From equation (13) and (14), it can be seen that the solubility is related to the heat of solution and the temperature at which the dissolving process takes place. When the dissolving process is endothermic, i.e. ΔH^0>0, a higher temperature results in a larger solubility. When the dissolving process is exothermic, i.e. ΔH^0<0, a higher temperature gives smaller solubility.

3 Semi-empirical Solubility Model

Equation (11) and (12) shows that there is potentially a linear relationship between $2\ln m$ and *1/T.* If such relationships can be identified, we may then be able to use these equations to analyse the solubility of both reactant and by-product of the $NaBH_4$ hydrolysis system and to develop a model to simulate and optimise the solution for the $NaBH_4$ hydrolysis system.

Figure 1 shows the measured solubility data of $NaBH_4$ at varying temperature [16, 18]. It can be seen that the solubility of sodium borohydride increases as the temperature increases. Below 36.4°C (309.4K), the crystalline state in the dissolution equilibrium is $NaBH_4\cdot 2H_2O$, and above this temperature the crystalline state in the dissolving equilibrium is $NaBH_4$. At 36.4°C (309.4K), two kinds of crystalline, $NaBH_4\cdot 2H_2O$ and $NaBH_4$, coexist in the saturated solution, which is regarded as the invariant point.

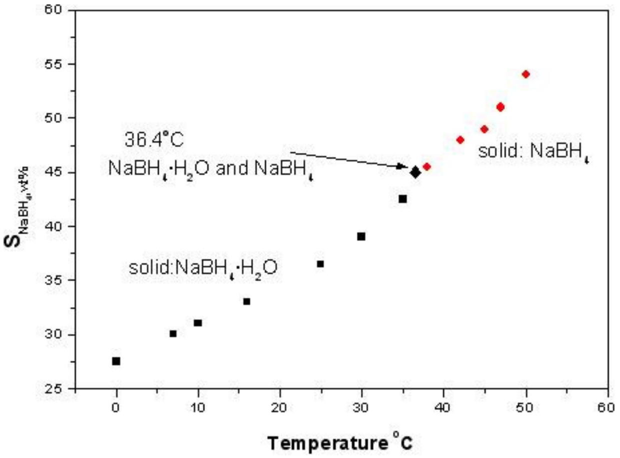

Fig.1 Measured solubility of $NaBH_4$ [16, 18]

Figure 2 shows the measured solubility of $NaBO_2$ at varying temperature [19]. There are two invariable points at 53.6°C and 105°C, respectively. These correspond to the transition temperatures of the sodium metaborate between its three crystalline states, $NaBO_2 \cdot 4H_2O$, $NaBO_2 \cdot 2H_2O$, and $NaBO_2 \cdot 1/2H_2O$. Overall, its solubility increases as the temperature increases up to the level of 105°C. This indicates that the enthalpy change of the dissolution is positive when the crystalline state is $NaBO_2 \cdot 4H_2O$ or $NaBO_2 \cdot 2H_2O$. If the solution temperature further increases, the solubility of sodium metaborate starts to decline.

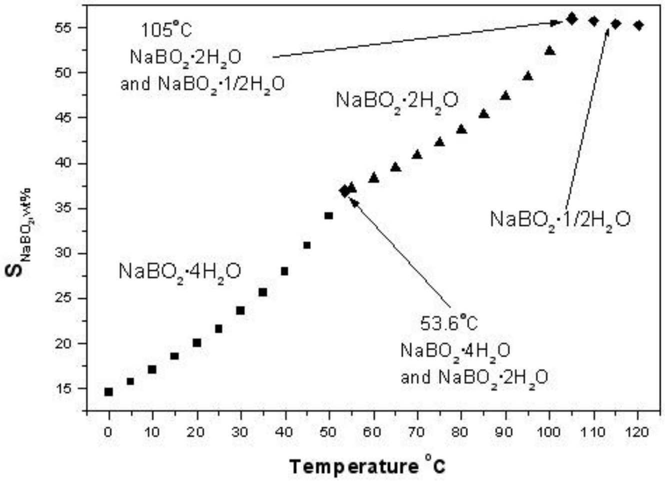

Fig.2 Measured solubility of $NaBO_2$ [19]

The solubility data cited in Figure 1 and 2 are in percentage by mass ($S_{wt\%}$). In order to obtain the parameters in the models, this needs to be converted into molality defined as

$$m = \frac{1000 S_{wt\%}}{(100 - S_{wt\%}) M} \quad (15)$$

where *M* is the molecular weight of $NaBH_4$ (equals to 37.83 g/mol) or $NaBO_2$ (equals to 65.8 g/mol).

Figure 3 and 4 shows the rearranged solubility data cited in Figure 1 and 2 by converting the mass solubility into molality in the form of $2\ln m$ vs. *1/T* for $NaBH_4$. It can be seen that a reasonable linearity exists at each temperature range. There are some differences between the measured data and the linear fit. This is probably mainly due to the fact that the water activity in the solution has been assumed to be constant at various $NaBH_4$ concentration and temperature. Further work in the area is undertaking.

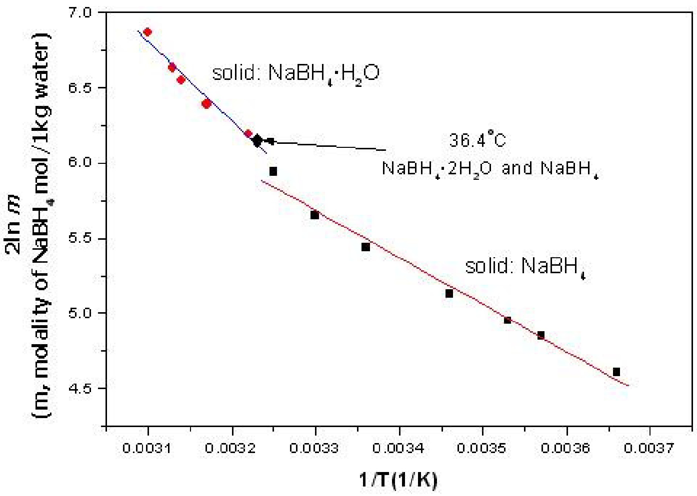

Fig.3 Temperature effect on $NaBH_4$ solubility

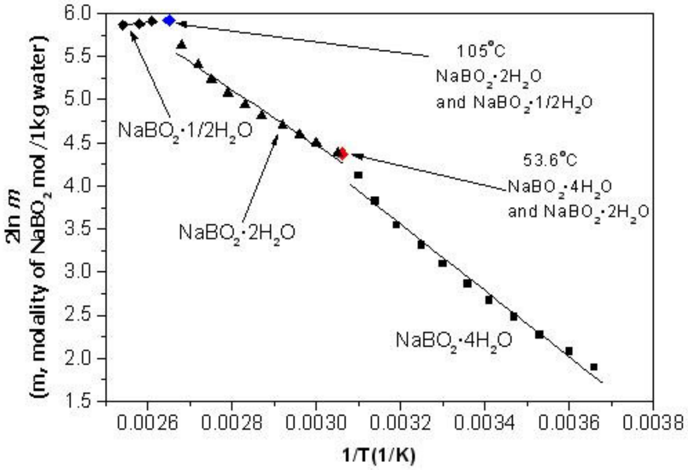

Fig.4 Temperature effect on $NaBO_2$ solubility

Comparing the linearity with the dissolution equilibrium theory, Eq.(11) and (12), both ΔH and constant *C* can be obtained. These are listed in Table 3. The positive value of the heat of solution suggests that the dissolving process is endothermic. Increasing temperature is favourable for the dissolution. On the other hand, the negative heat value indicates that the dissolution process is exothermic and increase in temperature will decrease the solubility of the solute.

Table 3 Semi-empirical parameters ΔH and *C*

Species		Parameters	
		ΔH^0 (kJ/mol)	Pre-exponential factor (Mol/kg water)
$NaBH_4$	$NaBH_4.2H_2O$ (<309.4K)	26.0	2980
	$NaBH_4$ ($\geq$309.4K)	43.7	10400
$NaBO_2$	$NaBO_2.4H_2O$ (<326.6K)	31.9	2750
	$NaBO_2.2H_2O$ (326.6-378K)	26.8	1180
	$NaBO_2.1/2H_2O$ ($\geq$378K)	-4.6	9.25

Substitute the heat and the constant into Eq. (15) and (16), the solubility of $NaBH_4$ and $NaBO_2$ in the form of percentage by mass at various temperature can then be obtained as

$$S_i = \frac{100E_i e^{-F_i/T}}{1000 + E_i e^{-F_i/T}} \tag{16}$$

where E_i and F_i are semi-empirical parameters listed in Table 4.

Table 4 Semi-empirical parameters E_i and F_i

Species		Parameters	
		E_i	F_i
$NaBH_4$	$NaBH_4.2H_2O$ (<309.4K)	1.13×10^5	1561
	$NaBH_4$ ($\geq$309.4K)	3.93×10^6	2629
$NaBO_2$	$NaBO_2.4H_2O$ (<326.6K)	1.81×10^5	1921
	$NaBO_2.2H_2O$ (326.6-378K)	7.76×10^4	1613
	$NaBO_2.1/2H_2O$ ($\geq$378K)	6.09×10^2	-277

Figure 5 and 6 show the comparison between calculated solubility using Eq.(18) and the measured value. It can be seen that a good agreements are obtained at all temperature ranges.

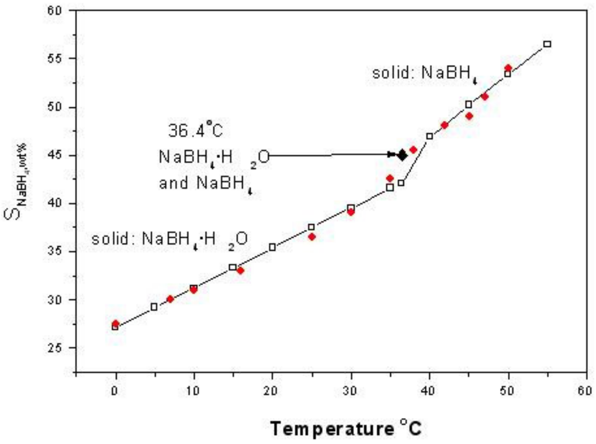

Fig.5 Comparison of calculated and measured solubility of $NaBH_4$

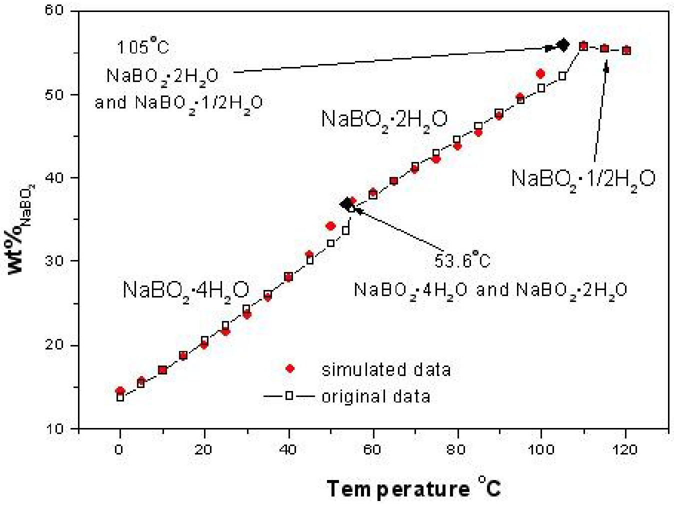

Fig.6 Comparison of calculated and measured solubility of $NaBO_2$

4. System Optimisation

In order to obtain the maximum possible hydrogen production density, the water contained in the $NaBH_4$ hydrolysis system needs to be optimised. There are three parts of water involve in the hydrolysis reactions: water used to produce a saturated $NaBH_4$ solution, w_1, water consumed by the hydrolysis reaction, w_2, and the water needed to dissolve and remove the by-product, w_3.

Table 5 listed the minimum amount of water required by each part of the requirement of the hydrolysis system at varying temperature ranges as shown.

Table 5 Water needed for $NaBH_4$ hydrolysis system

Temperature range (K)	Water in saturated $NaBH_4$ solution w_1 (g)	Water required for hydrolysis, w_2 (g)	Water required for dissolving $NaBO_2$, w_3 (g)	Water required by the system (w_2+w_3) (g)
273-309.4	102.0	36.0	180.0	216.0
309.4-326.6	47.0	36.0	130.0	166.0
326.6-378	30.0	36.0	60.0	96.0
>378	10.0	36.0	50	86.0

It can be seen that the amount of water needed to react with $NaBH_4$ and to solve the $NaBO_2$ is significantly larger than the amount of water contained in the saturated $NaBH_4$ solution. In other words, it is the water required to hydrolysis the $NaBH_4$ and dissolve the by-product $NaBO_2$ decides the optimised water content in the hydrolysis system. The optimised concentration of the system can thus be calculated by

$$\mathrm{C}_{\mathrm{NaBH}_4(wt\%)} = \frac{100 w_{\mathrm{NaBH}_4}}{w_2 + w_3 + w_{\mathrm{NaBH}_4}} \tag{17}$$

where w_{NaBH_4} is the weight of $NaBH_4$.

Figure 7 shows both calculated maximum optimised $NaBH_4$ concentration in the hydrolysis system and the concentration of saturated $NaBH_4$ solution at various temperatures. Two interesting phenomenon need to be addressed. First, the optimised concentration of $NaBH_4$ for the hydrolysis system is about half the level of saturated solution of $NaBH_4$. By simply looking at the concentration of the $NaBH_4$ to design the hydrolysis reaction system is clearly insufficient. Second, the optimised concentration increases as the solution temperature increases. This clearly increases the hydrogen production density. However, such benefit only exists when the solution temperature is lower than 378K. Further increase in temperature would decrease the optimised concentration, so reduces the hydrogen production density of the system. This is due to the fact that the dissolution of $NaBO_2$ at temperatures above 378K becomes exothermic and high temperature will reduce its solubility.

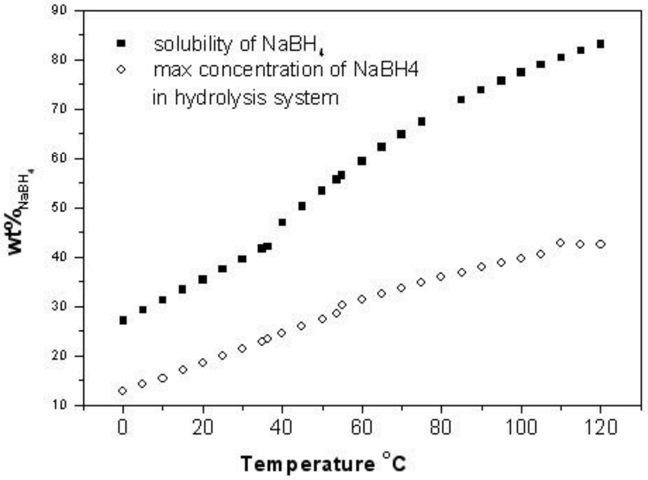

Fig.7 Calculated $NaBH_4$ solubility and its maximum concentration in the hydrolysis system

5. Conclusions

Based on the van Hoff's equation, a thermodynamic dissolution equilibrium model has been developed.

Using existing measured solubility data, a group of semi-empirical parameters required by the thermodynamic dissolution equilibrium model for $NaBH_4$ and $NaBO_2$ were obtained.

Using these semi-empirical parameters, the solubility of both $NaBH_4$ and $NaBO_2$ was predicted by the thermodynamic dissolution equilibrium model agrees well with the measured data.

The calculated results showed that the optimum concentration of the $NaBH_4$ solution used for the hydrolysis reaction is about half the level of its saturated solution. It increases as the solution temperature increases but only up to 378K. further increase in temperature will results in decrease in optimised concentration.

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