Experimental Study of the Thermal Effect of the Dissolution Reaction for Some Alkalis and Salts with Natural Mixing and Forced Stirring

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Abstract. The paper presents the results of an experimental study of the exothermal and endothermal effects occurring on the dissolution of potassium nitrate KNO_3 , ammonium nitrate NH_4NO_3 , potassium hydroxide KOH and sodium hydroxide NaOH, in distilled water with natural mixing and forced stirring. It is shown that for natural mixing, NH_4NO_3 and KOH are the most appropriate working substances for cooling and heat generation respectively, while for forced stirring, NH_4NO_3 and NaOH display better performance. The optimal concentrations of the liquid solutions for achieving extreme temperatures and maximal enthalpy changes are also defined. In addition, the regression function and regression coefficients describing correlations between the total enthalpy change of the calorimetric system and the solution concentration are found, for the most suitable liquid solutions. The experimental results obtained can be used to develop generating reactors for exothermal heating and endothermal cooling for a thermochemical seasonal storage system able to store solar heat or heat from combined heat and power (CHP) units of biogas plants in summer, for heating purposes in winter, while generating cooling to support air conditioning systems in summer.

1 Introduction

Recently, much research attention has been paid to the development of thermochemical heat storage systems, which may store the greatest amount of heat. Comprehensive reviews of the heat storage technology and the materials used are presented in [1-3]. However, according to Sole et al. [4], the main issue limiting the adoption of this technology was found to be the behavior of the working substances within the thermochemical reactor. Therefore, characterization of the working substances and the reactions occurring in thermochemical reactors will play a significant role in developing efficient heat storage systems.

In this experimental research, we have focused our attention on studying the dissolution reaction of chemicals in water, for substances that produce significant exothermal heat release and endothermal heat absorption, especially potassium hydroxide KOH, sodium hydroxide NaOH, ammonium nitrate NH_4NO_3 and potassium nitrate KNO_3 . The aim of our experiments was to study (1) the influence of the solution concentration on the solution temperature and enthalpy changes and (2) the influence of non-stirring and forced stirring on the thermal effect of the above-mentioned dissolution reactions, in order to find a suitable pair of working substances, as well as their concentrations, for a thermochemical heat storage and cooling generation system projected.

2 Experimental setup and measurement techniques

2.1 Description of the experimental setup and measuring equipment

A schematic and a photo of the experimental facility used to measure solution temperature change in the dissolution of alkalis and salts in water, are shown in **Fig. 1 a** and **Fig. 1 b** respectively. The setup included an insulated box (calorimeter) with a chemical test tube inside made of borosilicate glass, containing the solute. The tube was sealed by a rubber plug with three holes through it, used for the purposes of (1) distilled water inlet, (2) air outlet and (3) temperature sensor installation. In the experiments, the solution temperature was measured and automatically recorded using a measuring system consisting of (1) a HEL-705 (Honeywell) platinum temperature sensor calibrated with an accuracy of ± 0.5 K and installed in a hollow pipe made of 316 stainless steel, (2) a WAD-A-MAX (Acon) signal amplifier, (3) a WAD-AD-12-128HL (Acon) data logger and (4) a personal computer. To ensure a good thermal contact between the internal surface of the metal pipe and the temperature sensor, the former was filled with glycerin. The data acquisition frequency was set at 1 Hz.

Two types of experiments were conducted for each of the solutes. The first type consisted of measuring the

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temperature change of the solution when water was added to the solute without applying forced stirring, hereinafter called natural mixing. The second type was intended to

assess the influence of forced stirring on the solution temperature change. For forced stirring, a MM-5 (Ekochem) magnetic stirrer was used.

Fig. 1. Experimental setup: **a** – scheme of the experimental setup, **b** – photo of the experimental setup.

Distilled water was used as the solvent, while as the solute we tested four chemicals: two alkalis – KOH and NaOH, which produce significant exothermal heat release and two salts – NH_4NO_3 and KNO_3 , which produce considerable endothermal heat absorption. The distilled water was produced in our laboratory using a DE-4-2M (SZMO) distillation apparatus.

In each experiment, the initial temperature of the solutes and solvent was 10°C . The pressure inside the test tube was equal to the atmospheric pressure $P = 101 \text{ kPa}$. The total mass of the solution obtained in each experiment, i.e., solvent plus solute, was 150 g. The mass of the solute and solvent was measured using a FEN-300L (Dneproves) high-accuracy weighing machine.

2.2 Experimental procedure

The experimental procedure for studying the thermal effect of the dissolution reaction was as follows.

The glass test tube was first filled with the solute, sealed with a rubber plug and then installed in the insulated box. The data logger was triggered before adding the distilled water. The data acquisition system recorded the temperature of the solution formed over time. Five separate experiments were conducted to define the average values of the temperatures measured. Finally, Mathcad 15 was used for data processing and presenting the collected data using graphical representations.

The solution temperature change was measured for each of the solutes at varying concentrations from 10 mass % to 80 mass %. In the experiments with forced stirring, a magnetic stir bar was placed in the test tube before filling with the solute.

2.3 Procedure for calculating the enthalpy changes of the solutions

When calculating the enthalpy changes of the solutions, the following assumptions were made: (1) that the thermodynamic system under study was adiabatic, (2) that the liquid solution formed was a homogeneous mixture with a uniform temperature distribution throughout the volume, (3) that the specific heat capacity of the liquid solution is an additive property of the mixture and (4) that the enthalpy of mixing is zero.

To determine the specific enthalpy changes of solutions, hereinafter referred to as enthalpy changes, values of the solution temperature changes were used, which in turn were found from the temperature-time diagrams, as shown in **Fig. 2 a** and **Fig. 2 b** for endothermal and exothermal reactions respectively. Finally, the enthalpy change was calculated as the difference between maximal/minimal and initial solution enthalpies:

$$\Delta h_{sol} = h_2 - h_1, \left[\frac{\text{kJ}}{\text{kg}} \right], \quad (1)$$

where, h_1 is the solution enthalpy at the initial temperature t_1 and h_2 is the solution enthalpy at the maximal/minimal temperature t_2 , for exothermal and endothermal reactions respectively.

The total enthalpy change of the calorimetric system was found as the sum of the enthalpy change of the solution Δh_{sol} and the enthalpy change of the experimental sample setup consisting of borosilicate glass, 316 stainless steel and glycerin:

$$\Delta h_{total} = \Delta h_{sol} + \Delta h_{glass} + \Delta h_{steel} + \Delta h_{glyc}, \quad (2)$$

where, Δh_{glass} is the enthalpy change of the glass test tube, Δh_{steel} is the enthalpy change of the stainless steel hollow pipe and Δh_{glyc} is the enthalpy change of the glycerin.

Fig. 2. Examples of temperature-time diagrams for the endothermal and exothermal dissolution reactions:
a – 60% KNO₃ solution, b – 40% NaOH solution.

The enthalpy change of the borosilicate glass was estimated as follows:

$$\Delta h_{glass} = c_p^{glass} \cdot (t_2 - t_1), \quad (3)$$

where, c_p^{glass} is the specific heat of the borosilicate glass at 25°C, $c_p^{glass} = 830 \frac{J}{kg \cdot K}$ [5].

The enthalpy change of the stainless steel was calculated as follows:

$$\Delta h_{steel} = c_p^{steel} \cdot (t_2 - t_1), \quad (4)$$

where, c_p^{steel} is the specific heat of the 316 stainless steel in the temperature range 0-100°C, $c_p^{steel} = 500 \frac{J}{kg \cdot K}$ [6].

The enthalpy change of the glycerin was estimated as follows:

$$\Delta h_{glyc} = c_p^{glyc} \cdot (t_2 - t_1), \quad (5)$$

where, c_p^{glyc} is the specific heat of the glycerin at 25°C, $c_p^{glyc} = 2416 \frac{J}{kg \cdot K}$ [7].

The solution enthalpy at the initial temperature was defined as the sum of solvent and solute enthalpies, as shown below:

$$h_1 = c_p^{solute} \cdot t_1 + c_p^{solvent} \cdot t_1, \quad (6)$$

where, the first term is the enthalpy of the solute and the second term represents the enthalpy of the solvent at the initial temperature t_1 , c_p^{solute} is the isobaric specific heat capacity of the solute at t_1 , $c_p^{solvent}$ is the isobaric specific heat capacity of the solvent at t_1 and t_1 is the initial temperature of the solvent and solute.

The solution enthalpy at the maximal/minimal temperature was calculated as follows:

$$h_2 = c_p^{solution} \cdot t_2, \quad (7)$$

where, $c_p^{solution}$ is the isobaric specific heat capacity of the solution and t_2 is the maximal temperature of the solution for the exothermal reaction or the minimal temperature of the solution for the endothermal reaction.

According to [8], the specific heat capacity of the liquid solution is defined as an additive property, i.e.:

$$c_p^{solution} = [c_p^{solute} \cdot g + c_p^{solvent} \cdot (1 - g)], \quad (8)$$

where, c_p^{solute} is the isobaric specific heat capacity of the solute at t_2 , $c_p^{solvent}$ is the isobaric specific heat capacity of the solvent at t_2 and g is the mass fraction of the solute.

The specific heat capacities of solutes and solvent as a function of temperature were estimated as shown below:

- For KOH, the following formula was applied:

$$c_p^{solute} = \frac{c_{pmolar}^{KOH}}{M_{KOH}}, \quad (9)$$

where, c_{pmolar}^{KOH} is the molar specific heat capacity of KOH at constant pressure and M_{KOH} is the molar mass of KOH, $M_{KOH} = 40 \cdot 10^{-3} \frac{kg}{mole}$.

In turn, the molar specific heat capacity of KOH in the temperature range 50-522 K was calculated using the following expression [9]:

$$c_{pmolar}^{KOH} = -4.1 + 4.687 \cdot 10^{-1} \cdot t - 1.0706 \cdot 10^{-3} \cdot t^2 + 9.42 \cdot 10^{-7} \cdot t^3, \quad (10)$$

where, t is the temperature.

- For NaOH, the following expression was applied:

$$c_p^{solute} = \frac{c_{pmolar}^{NaOH}}{M_{NaOH}}, \quad (11)$$

where, c_{pmolar}^{NaOH} is the molar specific heat capacity of NaOH at constant pressure and M_{NaOH} is the molar mass of NaOH, $M_{NaOH} = 56.1 \cdot 10^{-3} \frac{kg}{mole}$.

In turn, the molar specific heat capacity of NaOH in the temperature range 60-592 K was calculated using the following expression [9]:

$$c_{pmolar}^{NaOH} = -31.8 + 8.455 \cdot 10^{-1} \cdot t - 3.0665 \cdot 10^{-3} \cdot t^2 + 5.0706 \cdot 10^{-6} \cdot t^3 - 2.92 \cdot 10^{-9} \cdot t^4, \quad (12)$$

where, t is the temperature.

- For NH₄NO₃, the isobaric specific heat capacity was calculated using two formulae [10]:

- in the temperature range -50-(-16.9)°C:

$$c_p^{solute} = 1.722 + 5.453 \cdot 10^{-3} \cdot t, \quad (13)$$

- in the temperature range -16.9-32.2°C:

$$c_p^{solute} = 1.625 + 4.714 \cdot 10^{-3} \cdot t. \quad (14)$$

- For KNO₃, the specific heat capacity was found by interpolation of the tabular data presented in [11].
- For H₂O, the following expression was used to calculate its isobaric specific heat capacity in the temperature range 0-100°C [12]:

$$c_p^{solvent} = 4223.6 + 1.075 \cdot t \cdot \ln\left(\frac{t}{100}\right), \quad (15)$$

where, t is the temperature.

3 Results and discussion

Examples of reaction coordinate diagrams of temperature versus time for KNO₃ and NaOH solutions are presented in **Fig. 2 a** and **Fig. 2 b** respectively. As was expected, in the dissolution reaction of alkalis in water, exothermal heat is released, resulting in a significant increase in the solution temperature, while the dissolution of salts generates cooling, resulting in a decrease in the solution temperature. Moreover, for all the chemicals under study, the use of forced stirring had a significant effect of increasing the exothermal heat release and endothermal heat absorption, which can be explained by better mixing of solute and solvent compared to the case of dissolution without stirring. In addition, forced stirring fosters the solubility of solutes, bringing forward the onset of extreme temperatures.

Diagrams of the extreme temperatures achieved versus solution concentrations, for KNO₃, NH₄NO₃, KOH and NaOH, are shown in **Figs 3 a, b, c and d** respectively.

Fig. 3. Extreme temperatures achieved in the dissolution reactions versus solution concentrations: **a** – KNO₃ solution, **b** – NH₄NO₃ solution, **c** – KOH solution and **d** – NaOH solution.

From the KNO₃ temperature-concentration diagram shown in **Fig. 3 a**, it can be seen that for natural mixing, an increase in the solution concentration results in a decrease in the solution temperature. In this case, the relationship between the minimal temperature achieved and the solution concentration is almost linear. However, dissolution of KNO₃ in water shows a slight endothermal effect. Here, the lowest temperature achieved is +3.5°C, at 70% solution concentration.

In contrast to the KNO₃ solution, for natural mixing NH₄NO₃ shows a much better endothermal effect, resulting in a more significant drop in the solution temperature (see **Fig. 3 b**). Thus, the lowest temperature achieved was -7.6°C at 60% solution concentration.

Furthermore, the relationship between the minimal temperature reached and the solution concentration is nonlinear.

Forced stirring for both liquid solutions, increases the endothermal effect, as shown in **Figs 3 a** and **3 b**. Thus, for KNO₃, the lowest temperature achieved is -1.5°C at 50% solution concentration, whereas for NH₄NO₃ the lowest temperature reached is -19.1°C at 50% solution concentration. It is interesting to note that for forced stirring, the maximal endothermal effect for NH₄NO₃ liquid solution is observed at 50% solution concentration, while without stirring, the optimal concentration is 60%.

Thus, in terms of the lowest temperature achieved, NH_4NO_3 can be regarded as a promising working substance for both mixing conditions.

As can be observed from the temperature-concentration diagrams shown in **Figs 3 c** and **3 d**, the dissolution reactions of KOH and NaOH in water are accompanied by considerable heat release, which results in a significant temperature change in the solutions formed. Thus, for the KOH solution, the optimal concentration for both mixing conditions is 70%, with a temperature increase of up to $+73.6^\circ\text{C}$ and $+86.5^\circ\text{C}$ for natural mixing and forced stirring respectively. For the NaOH solution, with natural mixing the maximal solution

temperature achieved is $+53.9^\circ\text{C}$ at 60% solution concentration, while for forced stirring it is $+80.5^\circ\text{C}$ at 40% solution concentration.

Along with values of the minimal and maximal temperatures achieved in the endothermal and exothermal dissolution reactions, solution enthalpy changes also play a significant role, since they give a practical definition of the specific storage capacities of the heat storage and cooling generation reactors.

Figs 4 a, b, c and **d** show the total enthalpy changes of the calorimetric system versus solution concentrations.

Fig. 4. Total enthalpy changes of the calorimetric system versus solution concentrations:
a – KNO_3 solution, **b** – NH_4NO_3 solution, **c** – KOH solution and **d** – NaOH solution.

Here, a negative sign “-” signifies endothermal heat absorption, whereas a positive sign “+” signifies exothermal heat release.

Comparing enthalpy-concentration diagrams for the KNO_3 and NH_4NO_3 solutions presented in **Fig. 4 a** and **Fig. 4 b**, it can be seen that with respect to the enthalpy change, NH_4NO_3 shows much better endothermal performance, since it can generate 2.1 and 2.3 times more cooling under natural and forced mixing conditions respectively. Thus, for natural mixing, the maximal endothermal heat absorption is about -144.7 kJ/kg at 60% solution concentration, while for forced stirring, the maximal endothermal heat absorption is about -223.5 kJ/kg at 50% solution concentration. That is to say, the use of forced stirring in the projected endothermal reactor may increase the cooling generation by 54%, together with a reduction of 10% in the NH_4NO_3 mass needed.

Comparing enthalpy-concentration diagrams for the KOH and NaOH solutions illustrated in **Fig. 4 c** and **Fig. 4 d**, it can be seen that for natural mixing, the dissolution of KOH in water generates the maximal exothermal heat of 340.9 kJ/kg at 70% solution concentration, while the dissolution of NaOH is accompanied by a release of 247.3 kJ/kg of exothermal heat at 60% solution concentration. Therefore, for natural mixing, the dissolution of KOH generates 38% more heat than the dissolution of NaOH. However, under forced mixing conditions, NaOH displays better performance: 460.8 kJ/kg of exothermal heat is released at 40% solution concentration versus 419.9 kJ/kg of exothermal heat released at 50% solution concentration for KOH. Thus, in terms of the solution

enthalpy change, KOH is more appropriate for exothermal heat generation with natural mixing, while NaOH is more suitable with forced stirring.

It also should be noted that, despite the fact that the highest temperature is achieved for the dissolution of KOH, NaOH generates greater enthalpy changes, even at lower temperatures, which can be explained by the higher specific heat capacity of NaOH.

In addition to the diagrams produced, a regression function with regression coefficients was defined for each

Table 1. Regression coefficients for the function describing the correlation between the total enthalpy change of the calorimetric system and the solution concentration.

Regression coefficients	NH ₄ NO ₃		KOH		NaOH	
	mixing conditions		mixing conditions		mixing conditions	
	natural	forced	natural	forced	natural	forced
	accuracy		accuracy		accuracy	
	99.4%	98.9%	98.8%	99.4%	99.8%	99.7%
a ₀	-64.293	-7.843	-7.593	-35.85	-43.236	-167.9
a ₁	0.748	-7.606	8.458	12.983	13.107	38.726
a ₂	-0.076	0.063	-0.045	-0.018	-0.183	-0.741
a ₃	7.154·10 ⁻⁴	1.359·10 ⁻⁴	-1.364·10 ⁻⁴	-1.152·10 ⁻³	7.326·10 ⁻⁴	3.968·10 ⁻³

of the solutions and mixing conditions, as given below. For this purpose, the optimized Levenberg-Marquardt method in Mathcad 15 was applied.

$$\Delta h_{total} = a_0 + a_1 \cdot c + a_2 \cdot c^2 + a_3 \cdot c^3 \quad (16)$$

where, c is the solution concentration (m%) and a_0 , a_1 , a_2 and a_3 are the regression coefficients, with values as presented in **Table 1**.

Conclusions

In this paper, an experimental study has been carried out with the aim of investigating the thermal effects occurring in the dissolution of some alkalis and salts in water, under natural mixing and forced stirring conditions. On the basis of the results obtained, the following conclusions can be drawn.

- For endothermal cooling generation, NH₄NO₃ is the most suitable solute, since the dissolution of NH₄NO₃ in water can produce significant endothermal heat absorption accompanied by a considerable solution temperature drop. Thus, for natural mixing, the maximum cooling generation occurs at 60% solution concentration with a temperature drop of up to -7.6°C, with -144.7 kJ/kg of heat absorbed. With forced stirring, the maximal endothermal effect is observed at 50% solution concentration with a temperature drop of up to -19.1°C and -223.5 kJ/kg of cooling generated.

- Under natural mixing conditions, KOH is more appropriate for exothermal heat generation, as the dissolution of KOH in water increases the solution temperature by up to +73.6°C and releases 340.9 kJ/kg of exothermal heat at 70% solution concentration. Under forced stirring conditions, NaOH displays better performance, with a temperature rise of up to +80.5°C and 460.8 kJ/kg of exothermal heat released at 40% solution concentration.

The experimental results obtained in this study will be used to improve the design and efficiency of exothermal heating and endothermal cooling generation reactors in thermochemical storage systems. We also intend to study the heating and cooling generation abilities of these pairs of working substances under vacuum conditions.

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