Hydration characteristics of lithium, zinc, potassium and sodium salts

E. Lefebvre[1], S. Bennici[1], E. Gagnière[2], D. Mangin[2], and A. Auroux[1]

[1]Université de Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, F-69626 Villeurbanne, France
[2]Université de Lyon 1, CNRS, UMR 5007, LAGEP, Laboratoire d'automatique et de génie des procédés, CPE Lyon, 43 boulevard du 11 Novembre 1918, 69100 Villeurbanne, France

1 Introduction

A new inter-seasonal process for storing solar energy is based on absorption of water by a saline solution [1]. For this purpose, many salt hydrates proposed for thermal energy storage application have been studied. In a previous study [2, 3], it was proved that crystallization of the solution inside a storage tank was necessary to increase the storage density, and thus reduce the storage tank size and cost. Crystallization is possible due to a little circulation of fluid in the tank [4] and it must be reversible and controlled.

Enhancement of the storage capacity can be the increase of the mass fraction of absorbent in the concentrated solution. Another criterion taken into account in this process is the appearance (size and form) of the crystals which can impact on the design of the storage tank. As a consequence, the salt needs to be in an anhydrous or at least monohydrate form at the crystallization temperature (278 K). The first salt chosen for the system was lithium bromide. It presents interesting thermal properties. However, LiBr crystallizes in dihydrated form at the temperature of the storage tank surrounding (5-10°C) with a water content of 29 wt% of water [2-5]. In view of replacement of LiBr, it was selected six other salts according to their literature data on their hydrated forms at low temperature, their solubility in water and their low price. These salts are lithium chloride, zinc bromide, potassium hydroxide, potassium formate, sodium hydroxide and sodium thiocyanate. Lithium chloride is a well-known desiccant salt principally used in absorption system for cooling and dehumidification [6]. Because of their good thermal properties, potassium formate and sodium hydroxide were previously studied respectively as a secondary refrigerant in an aqueous solution [7] and as the sorbent in a long term heat storage process. Flamensbeck [8] associated potassium hydroxide with sodium hydroxide to replace lithium bromide in absorption chiller. Eventually, sodium thiocyanate was generally combined with ammonia to create the couple absorbent/absorbate as a refrigerant in absorption cooling system [9].

In this work, hydration characteristics, enthalpies and transition temperature, of these seven salts, were determined using a thermogravimetry analysis (TG) and differential scanning analysis (DSC). Results of these experiments were compared to those of lithium bromide.

2 Experimental

2.1 Samples preparation

Anhydrous salts were purchased from Alfa (LiBr, KOH and NaOH) or Sigma Aldrich (LiCl, $ZnBr_2$, $KCHO_2$ and KSCN) with purity between 99.9% and 99.99%.

Hydrated salts were prepared from anhydrous salts at room temperature. For all salts except $ZnBr_2$, the hydrated forms were prepared under a saturated water atmosphere which was created by a hermetical batch containing a little amount of water. The water composition of the salts was regularly followed by mass variation in order to obtain a stable hydrated form in accordance with theoretical data. This method was used to create the hydrated salts presented in Table 1.

Because of its high kinetics of hydration, the di hydrated form of zinc bromide was obtained by precipitation. The anhydrous salt was solubilised in water at 323 K and crystallised at room temperature. The solution was filtered and dried at 298 K. All hydrated salts were kept in a desiccator over silica gel and then analysed both by TG and DSC.

Table 1. Hydrated form of the prepared salts.

Salt	Hydrates formed
LiBr	$LiBr.2H_2O$
LiCl	$LiCl. H_2O$
KOH	$KOH.2H_2O$
$KCHO_2$	$KCHO_2. H_2O$
NaOH	$NaOH. H_2O$
NaSCN	$NaSCN.2H_2O$
$ZnBr_2$	$ZnBr_2. 2H_2O$

2.2 DSC analysis

DSC measurements were carried out with a DSC Q100 from TA Instruments. Data were integrated from the recorded output computational software. The instrument was calibrated and tested with a high purity indium metal. Due to their high ability to absorb moisture when exposed to air, the samples were loaded and sealed quickly. About 1 to 5 mg of salts were introduced into an aluminium sealed-type DSC pan. A hole of c.a. 0.5 mm in diameter was made in the top of the sealed pan to evacuate the water evolved during the dehydration. The flow of dry nitrogen was maintained constant at 50 cm^3/min to get a stationary vaporization [10].

Samples were heated from 274 K to either 473 K or 573 K (depending on their melting temperature) with a heating rate of 5 K/min. This temperature was maintained one minute and then samples were cooled to 274 K at 15 K/min. Endoh [10] explained that a thin film of salt crystallite takes place over sample during heating because of the high enthalpy of vaporization of water which created a temperature gradient on samples. In order to avoid this phenomenon, samples were placed on the pan, uniformly centred and with a very small thickness.

These analyses proved the transition temperatures of hydrated forms and their associated enthalpies.

2.3 TG analysis

The TG analyses were performed with a HI RES Modulated TGA2950 TG Analyzer from TA Instruments. The temperature calibration was made with a high purity indium sample by correspondence with its Curie temperature.

Around 5 mg of sample were quickly placed into an opened platinum pan and immediately analysed. The flow rate of dry nitrogen was 90cm^3/min. In order to compare these data with DSC analyses, the samples were heated to 473 K or 573 K with a rate of 5 K/min. The data allowed to determine the loss of water corresponding to each transition observed in DSC.

3 Results

TG and DSC results were treated simultaneously for all samples. The temperature transitions observed by DSC are very similar to those determined by TG analysis. The results for all salts are reported in Table 2.

Two different transitions were observed for lithium bromide corresponding to the transitions LiBr.2H$_2$O/LiBr.H$_2$O and LiBr.H$_2$O/ anhydrous LiBr. Apelblat [11], by analysis of the phase diagram of the (lithium bromide + water) system, determined a temperature "T$_{literature}$" corresponding to the different forms of LiBr in equilibrium with their saturated aqueous solution. These literature temperatures are reported also on Table 2.

Transition temperatures are in good agreement with the literature. Moreover, the enthalpies of transition of the hydrated forms were calculated by integrating the peaks on DSC plot.

A little exothermic peak without any mass variation is observed by DSC near 305 K. It is due to an α → β transformation of LiBr.H$_2$O, as indicated on the phase diagram [10].

The transition temperature of LiCl.H$_2$O into anhydrous LiCl is 363 K in agreement with that given by the phase diagram of (LiCl + H$_2$O) [12] and Apelblat [13].

The phase diagram of potassium hydroxide − water [14] and sodium hydroxide-water [7] presented different hydrated transition temperatures. These values were compared to the transition temperatures determined by TG analysis of KOH.2H$_2$O and NaOH.H$_2$O. DSC confirmed the temperature values presented in Table 2. It can be noticed that enthalpies corresponding to the transition between monohydrate and anhydrous forms is the same for both hydroxide salts.

Transition temperature of NaSCN-NaSCN.2H$_2$O was compared to data given by Nyvlt [15]. He assessed that this temperature corresponded to the transition between the dihydrate and anhydrous forms. Our measured temperature corresponded to this transition and is in good accordance with the data given by Nyvlt.

Little information is available on the properties of the hydrated forms of potassium formate which prevented us from a comparison with literature data.

**Table 2.** TG and DSC results for all salts.

Forms of salts	Transition temperature during heating (K)		ΔH (J/g)
	T$_{literature}$	T$_{exp}$	
LiBr	>432 [11]		434	32
LiBr.H$_2$O	316 [11]	313 [15]	315	31
LiBr.2H$_2$O	<281 [11]	277 [15]	-	-
LiCl	373 [13]	369 [15]	367	89
LiCl.H$_2$O	293 [12]	292 [15]	-	-
LiCl.2H$_2$O			-	-
KOH	372 [14]		375	78
KOH.H$_2$O	306 [14]	306 [15]	313	-
KOH.2H$_2$O	240 [14]		-	-
NaOH	335 [7]	335 [15]	337	78
NaOH.H$_2$O	285 [7]	285 [15]	-	-
NaOH.2H$_2$O	278 [7]		-	-
NaOH.3.5H$_2$O	277 [7]	278[15]	-	-
KCHO$_2$			438	63
KCHO$_2$.H$_2$O			-	-
ZnBr$_2$		308 [15]	304	14
ZnBr$_2$.2H$_2$O			-	-
NaSCN		303 [15]	309	56
NaSCN.2H$_2$O			-	-

4 Conclusion

Firstly, transition enthalpy between hydrated and anhydrous forms indicated the strength of interaction between solute and water. The lowest is this enthalpy; the most convenient is the salt in the process. Transition enthalpy of lithium chloride between monohydrate and

anhydrous forms is deeply higher than that of lithium bromide.

Secondly, according to the hydrated form of salts, the mass fraction of water in the storage tank can be calculated. Figure 1 shows water content of the solution in the storage tank at 278 K and room temperature for the seven salts.
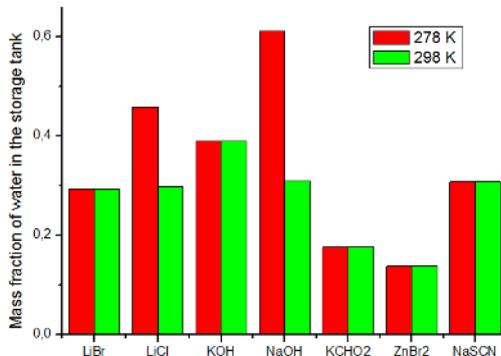
Figure 1. Water content of the solution in the storage tank for all salts at 278 K and 298 K.

In the light of these results, zinc bromide and potassium formate are the most suitable sample for the process. Both solutions in the storage tank reach the lowest water content, 14 wt% for $ZnBr_2$ and 18 wt% for $KCHO_2$. Besides, they present low transition temperature and associated enthalpy. Moreover, potassium hydroxide and sodium thiocyanate present small mass fraction of water in the solution but a high transition enthalpy can be noticed. No enhancement on the storage capacity can be realized with lithium chloride and sodium hydroxide which mass fractions of water are respectively 30 and 31 wt%. Zinc bromide seems to be the most performing salt which can be used in the inter-seasonal process.

References

1. H. Lui, Ph.D. dissertation, University of Savoie, 2010
2. K.E. N'Tsoukpoe, N. Le Pierrès, L. Luo, Energy **37** 346 (2012)
3. P. Tatsidjodoung, N. Le Pierrès, L. Luo, Renewable and Sustainable Energy Reviews **18** 327 (2013)
4. L. Hui, K.E. N'Tsoukpoe, N. Le Pierrès, L. Luo Energy Conversion and Management **52** 2427 (2011)
5. K.E. N'Tsoukpoe, N. Le Pierrès, Energy Procedia **30** 331 (2012)
6. C. Bales, Laboratory prototypes of thermo-chemical and sorption storage units, Report B3-Task 32 (2007). Available from: http://www.iea-shc.org/publications/downloads/task32-Laboratory_Prototypes_of Thermo-Chemical_and_Sorption_Storage_Units.pdf
7. R. Weber, V. Dorer, Vacuum **82** 708 (2008)
8. M. Flamensbeck, F. Summerer, P. Riesch, F. Ziegler, G. Alefeld, Applied Thermal Engineering **18** 413 (1998)
9. A. Acuna, N. Velazquez, J. Cerezo, Applied Thermal Engineering **51** 1273 (2013)
10. K. Endoch, H. Suga, Thermochimica Acta **327** 133 (1999)
11. A. Apelblat, A. Tamir, Journal of Chemical Thermodynamics **18** 201 (1986)
12. J. Patek, J. Klomfar, Fluid Phase Equilibria **250** 138 (2006)
13. A. Apelblat, R. Weintraub, A. Tamir, Journal of Chemical Thermodynamics **16** 935 (1984)
14. W.M. Vogel, K.J. Routsis, V.J. Kehrer, D.A. Landsman, J.G. Tschinkel, Journal of Chemical and Engineering Data **12** 465 (1967)
15. J. Nyvlt, *Solid-Liquid Phase Equilibria*, Elsevier Scientific Publishing Company, New York (1977)