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Thermal evaluation of molten salts for solar thermal energy storage

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Abstract

Molten salts are known for having good heat transfer properties to be used in thermal storage. This application has become important in the development of thermal technologies for solar energy concentration. The operating principle of these technologies is based on the concentration of sun rays by mirrors to achieve high temperatures and aims to operate turbines coupled with electric generators to produce electricity.

Therefore, alkali nitrates and sodium nitrite are good candidates due to the low melting point and excellent heat capacity. These properties produce a broad molten salt operating range and enable effective thermal storage in solar power plants. But one of the critical parameters is the degradation because the cyclic process of heating / cooling. It is important to study the thermal properties in order to determine the operating conditions and lifetime during processing.

The purpose of this study is to evaluate the melting point and thermal stability of conventional salt systems, such as the Solar Salt (60% $NaNO_3$- 40% -KNO_3, Tm = 220 °C) and HITEC (7% $NaNO_3$- 53% KNO_3- 40%$NaNO_2$, Tm = 142 °C), and a novel eutectic mixture. The physical and chemical properties of the studied salts were evaluated by Differential Scanning Calorimetry **(**DSC), Thermogravimetric Analysis (TGA) and morphology was observed in SEM images. In order to compare experimental results with theoretical calculations, the eutectic temperature and heat capacity were calculated with Factsage® thermodynamic software.

Melting point was found to be lower than that of conventional salts due to the Lithium Nitrate addition in the systems.

Key words

Molten salts, eutectic mixture, thermal storage, thermal stability, solar thermal collectors.

1. Introduction

It is well known that thermal energy storage (TES) can replace heat and coal production from fossil fuels and reduce CO_2 emissions. Therefore, TES technologies are a key factor in solar thermal power plants [1]. Using heat transfer fluids (HTS), electricity can be generated even when sunlight is not available. Several organic materials as oil and inorganic materials as molten salts have been proposed to be used as potential HTF and thermal energy storage media. However, TES technologies face some barriers to become competitive in terms of costs in comparison with the conventional technologies. For this reason, materials used as storage media need improvements in thermal stability which is associated with material properties.

Molten salt mixtures are being used to improve the energy conversion efficiency and reduce the cost of electricity production [2]. Low melting point, low viscosity, low vapour pressure, with high heat capacity and thermal stability are the most important characteristics to be considered in a salt system for thermal energy storage and heat transfer applications. Commercial Solar Salt and HITEC [3] [4] salts are available that provide some of these characteristics and are being used in solar thermal plants in Spain and United States.

With this research, the thermal stability of molten salts and the evaluation of thermodynamic properties are highlighted, as well as the utilization of FactSage® thermodynamic software to confirm from the experimental results, the melting point and heat capacity of the salts studied.

2. Experiment

2.1. Materials and synthesis

All the salt systems obtained from Panreac were prepared in a laboratory scale of 3-5 g of each system. The salts were mixing in a reagent grade according to the composition obtained from the Factsage modeling. Binary and ternary systems were preparing by the well know *mix and split* method using in combinatory chemistry and developed by Áprah Furka [5]. Weighted percentages of salts were heated in a stainless steel beakers and placed on a furnace at a temperature of

220 ºC during 2h to melt and homogenize the samples. The molten salts were maintained at 220 °C after melting until it was removed in pellets from the furnace and allowed to cool to room temperature in a dessicator. Then the solidified salts were ground into powder to be characterized by DSC, TGA and SEM.

2.2. Apparatus and procedure

A Differential Scanning Calorimeter (DSC Q200) was used to measure the melting point and heat capacity of the eutectic mixtures. The measured were made in Modulated Mode in order to obtain reliable heat capacity results. The modulated ramp was made to ± 1.00 °C every 70 s and the ramp was 3.00 °C/min to 290.00 °C.

After measuring the melting point, 10-12 mg of each sample was placed onto a platinum pan. The pan was loaded into the TGA Q500 and the temperature was ramped from ambient to 900 °C at 15 °C/min using air as the purge gas. With TGA test the maximum temperature or thermal stability of a molten salt system and losses were measured.

3. Results

FactSage thermodynamic software has been used to perform the calculation of the phase diagram. With the phase diagrams obtained, information about what phases are present, the state of those phases and the relative quantities of each phase give us the basis for predicting the changes in internal structure of molten salts that will be used as thermal storage media.

The program calculates liquidus temperatures over the different compositions of the system. The input parameters are the single salt components and the temperature range to be evaluated. Table 1 lists the values of melting temperature for the single salts studied. In our case, the temperature range was between 25-600 ºC.

Component	Tm (ºC)
$NaNO_3$	306
KNO_3	334
$NaNO_2$	271
$LiNO_3$	264

Table 1. Melting temperature for the single salts.

Figure 1 shows the phase diagram of the mixture $NaNO_3$-KNO_3-$LiNO_3$. The triple point is the eutectic which has the lowest temperature in all the system (122.58 ºC). DSC confirms the peak temperature which corresponds to complete melting given by the simulation.

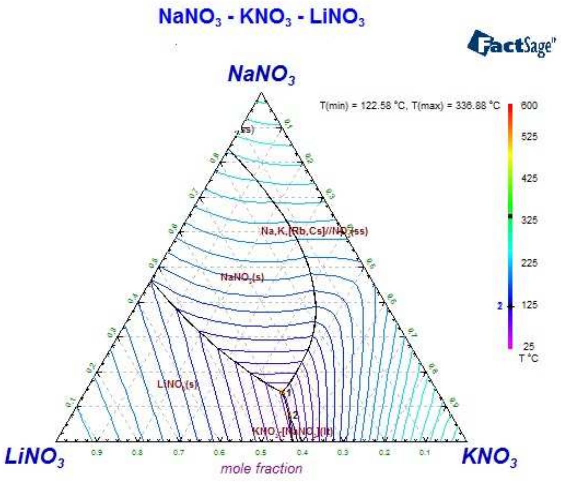

Fig. 1. Phase diagram of $NaNO_3$-KNO_3-$LiNO_3$

In melting point and heat capacity determination, Differential scanning calorimetry (DSC) was used. Table 2 shows a comparison of melting point and heat capacities of different systems. A solid- solid transition and various endothermic peaks were identified with one heating/cooling run. But after 3 runs, only one endothermic peak was identified which was considered as the melting for all systems. So the complete mixing can only be achieved after 3 runs. The melting point of the experimental salt mixtures with $LiNO_3$ are much lower than that of conventional binary solar salt. Several authors have treated the cation size as major reason of difference in the behavior of molten nitrates.

It is noted that heat capacity is an average of specific heat capacities for temperatures between the solid- liquid transitions. At this point, the maximum value was found and this parameter increases with temperature that is attributed to the high atomic mobility in the liquid state.

Eutectic mixture	Tm (ºC)	Heat capacity (J/g.ºC)
Conventional Solar Salt	220	2,15
HITEC salt	142	2,23
Novel mixture with 15%$LiNO_3$	104	2,46
Novel mixture with 20%$LiNO_3$	79	2,78

Table 2. Comparison of melting points and heat capacities for the eutectic systems studied.

The thermal stability of the salts was determined by using TGA from 25 to 900ºC under air with the fixed flow rate as 90 ml/min. Table 3 shows a comparison of temperatures which weight losses appear of conventional solar salt, HITEC salt and quaternary eutectic salt mixtures with $LiNO_3$. Fig. 2 shows the temperature at which rapid weight loss begins for the HITEC salt (625,38 ºC).

For all systems a weight loss was observed at ~ 100ºC due to the presence of water, especially for $LiNO_3$ that becomes hygroscopic especially with 20% weight percentage. Total weight loss for all systems was calculated to be ≤ 3% which indicates the thermal stability of molten salts under temperatures above 500ºC.

Melting point, heat capacity and thermal stability are affected by multiple parameters. With $LiNO_3$ eutectics mixtures the lower melting point and higher heat capacity were obtained but the thermal stability is not improved due to the weight losses below 580ºC in comparison with a degradation temperature about 625ºC for the commercial HITEC salt.

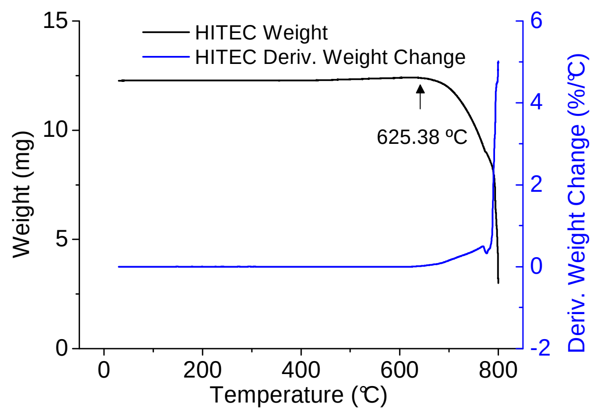

Fig. 2. TG curve for decomposition of $NaNO_3$-$NaNO_2$-KNO_3 HITEC mixture.

Eutectic mixture	Degradation temperature(ºC)
Conventional Solar Salt	511,77
HITEC salt	625,38
Novel mixture with 15%$LiNO_3$	579,72
Novel mixture with 20%$LiNO_3$	560,93

Table 3. Comparison of degradation temperature of conventional solar salt, HITEC salt and quaternary eutectic salt mixtures with different $LiNO_3$ contents.

After preparing the salts systems as described above, SEM was used to examine the morphology of those salts. The salt crystals formed after melting are confirmed by the EDX analysis in a homogenous mixture with nitrogen, oxygen, sodium and potassium.
Images in Figure 2 show formed cubes in a $NaNO_3$-KNO_3 binary system a) and b) is from Solar salt composed by $NaNO_3$- KNO_3, and c) correspond to the commercial salt composed by $NaNO_3$, $NaNO_2$ and KNO_3 which are in the same proportion after the EDS measurements. Also the nitrite formation, NO_2, is favored compared to nitrate, NO_3. It is important to highlight that cycles are very important to obtain a homogeneous salt component. After 3 heating cycles, a salt solution is formed but five or more cycles are recommended. Image d) shows the novel composition with 15% $LiNO_3$ where small agglomerates are formed and the cubes have more rounded edges in comparison with the others.

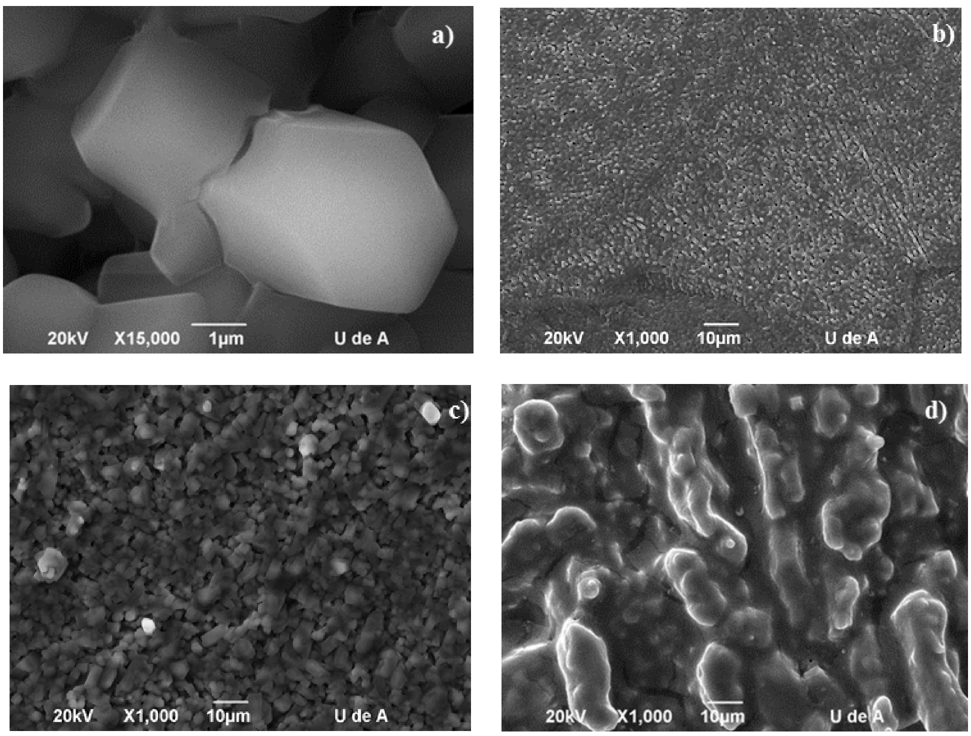

Fig. 3. SEM images showing morphology of molten salts.

4. Conclusions

Thermodynamic modeling is a very essential tool to predict salt mixtures properties, allowing the study of already optimized systems in order to save time and resources.

Low melting point with high heat capacity and excellent thermal stability are the important characteristics to be considered in a salt system for thermal energy storage and heat transfer applications.

DSC was used to test the experimental melting point of the quaternary systems which are lower than the conventional salts. The heat capacity of the quaternary system was also detected using DSC and found values 2,78 J/g.ºC with the $LiNO_3$ as a quaternary component in comparison with 2,21 J/g.ºC for the binary solar salt system.

In the thermal stability experiment using TGA, the upper temperature for thermal stability of the eutectic mixtures was found to be 625,38 ºC corresponding to HITEC solar salt. Also, weight losses corresponds to thermal decomposition of the salt mixtures were calculated to be ≤ 3% for all systems which indicates the thermal stability of molten salts under temperatures above 500ºC.

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