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A new ternary chloride eutectic mixture and its thermo-physical properties for solar thermal energy storage

Xiaolan Wei a*, Ming Song a, Qiang peng c, Jing Ding b, Jianping Yang a

a School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
b School of Engineering, Sun Yat-sen University, Guangzhou High Education Mega Center, Guangzhou 510006, PR China
c School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan 528458, PR China

Abstract

In order to meet the needs of solar energy storage over 550°C, the eutectic point and composition of a new ternary salt mixture consisted of NaCl, CaCl₂ and MgCl₂ was predicted from calculated phase diagram and that was also validated by differential scanning calorimetry (DSC). The lowest eutectic temperature predicted by the phase diagram was 424.05°C. The actual eutectic point was confirmed 424°C but with different composition compared with the predicted eutectic point. Besides, this new eutectic salt mixture (named SYSU-C4) was prepared by static melting method and its thermo-physical properties were also measured. Heat capacity, density and viscosity of SYSU-C4 were respectively determined by DSC, Archimedes and vibration-rotation methods. Heat capacity of this molten salt was calculated from DSC curve in the reference of sapphire standard material, the average value of solid salt was 0.83 J/g K and the liquid salt was 1.19 J/g K. Density of molten salt decreased linearly from 2.5 g/cm³ to 1.9 g/cm³ with increasing in the temperature range from 500°C to 750°C. Viscosity of the eutectic salt mixture also decreased from 4.0 cp to 3.0 cp as the temperature increased. Meanwhile, mass loss curves under isothermal conditions were determined and the result showed that the thermal stability of this new eutectic salt was excellent under 700°C.

Keywords: ternary eutectic mixture; diagram; thermo-physical properties; thermal stability

1. Introduction

Molten salts have been widely used as heat transfer fluid for solar energy storage [1-3]. Molten nitrate salts are not stable enough over 500°C and that restricts their application at temperature over 550°C. Chlorides are attractive due to their low cost, high latent heat, appropriate operating temperature (400-850°C), good thermal stability. They’re still promising to be favorable thermal energy storage medium although with a little high corrosiveness [4]. A new ternary chloride molten salt system composed of NaCl, CaCl₂ and MgCl₂ has been designed through calculating its phase diagram [5]. DSC curve of the predicted eutectic salt mixture showed that the actual melting point had little difference with that predicted value, which was mainly attributed to the deviation of calculated eutectic composition. Besides, ternary salt mixtures with different compositions near the predicted eutectic point were prepared and the true eutectic salt mixture was confirmed in this paper. The eutectic salt mixture used as solar energy storage was prepared basing on the confirmed true eutectic composition. All of the relevant properties of this mixture such as heat capacity, density, viscosity and thermal stability were determined in order to examine whether this eutectic salt mixture was suitable for the solar thermal energy storage application.

2. Experiment section

The salt mixtures for determining the actual eutectic composition were prepared by mixing the three components according to the compositions near the predicted eutectic point. The mixtures were respectively static heated to 600°C, held for 3h to ensure a homogeneous mixture and then cooled to ambient temperature. The solidified salt mixture was ground into powder using mechanical rolling, sealed and kept in desiccators.

* Corresponding author. Tel.: 086-87111834
E-mail address: xhwei@scut.edu.cn.
STD 449°C differential scanning calorimetry (DSC, Germany NETZSCH Company) was used to confirm the true eutectic point of ternary system. About 5-10mg samples were put into alumina crucible with a reference empty one. The measurements were conducted in purified nitrogen atmosphere with a flow rate of 100mL/min and at a heating rate of 20K/min to 800°C.

Subsequently, thermal-physical properties of the confirmed eutectic molten salt mixture (named SYSU-C4) were obtained. Heat capacity was determined from DSC curve in the reference of sapphire standard material. Density was gained by Archimedes theory in RSD-06 synthetic test instrument. Viscosity was measured with vibration-rotation high temperature melt viscosity instrument (Japan Tokyo Kabushiki Kaisha). About 40g SYSU-C4 were put in alumina crucible to test the thermal stability, the crucible was covered with a lid in order to avoid the moisture and reduce the volatilization of chloride during the test.

3. Results and discussion

3.1. Determination of molten salts’ lowest eutectic point

The calculated ternary phase diagram is graphically presented in Fig.1 [5]. The predicted eutectic point should be validated by experiments. The amplified DSC curve of predicted eutectic mixture between 350°C and 500°C is given in Fig.2 and that shows two overlapping endothermic peaks, which demonstrates that the eutectic composition predicted by calculated phase diagram had a little deviation. Therefore, the undoubted eutectic salt mixture with lowest melting point was identified near the predicted eutectic composition. The DSC curve was presented in Fig.3 and it shows single smooth endothermic peak. The melting point of this salt mixture was tested 424°C, which was in excellent agreement with that predicted value 424.05°C. The latent heat of melting for molten salt was nearly 190J/g, which is super for thermal energy storage. Then, thermal properties of this true eutectic molten salt (named SYSU-C4) were measured in the next sections.

![Fig. 1. Phase diagram of the ternary system (NaCl-CaCl2-MgCl2)](image)

![Fig. 2. DSC curves of predicted eutectic mixture](image)

![Fig. 3. DSC curves of SYSU-C4](image)

3.2. Heat capacity

Heat capacity of SYSU-C4 in nitrogen was presented in Fig.4 and compared with the available data in the literature [6]. The experimental results can be divided into two section; solid state (246.85-406.85°C) and liquid state (476.85-626.85°C). The heat capacity data of each state could be fit to a polynomial equation.
The heat capacity data for SYSU-C4 in the solid state in the temperature range of 226.85 to 406.85°C is fit to a second order polynomial equation:

\[ C_p (\text{Solid}) = 4.5759 \times 10^{-5}T^2 - 0.02756T + 4.7954 \text{ (J/g °C)} \]

The R² value for this fit was greater than 0.97. The average heat capacity of the solid SYSU-C4 is 0.83 J/g K.

The heat capacity data for SYSU-C4 in the liquid state in the temperature range of 476.85 to 626.85°C can be also fit to a second order polynomial equation:

\[ C_p (\text{liquid}) = 4.0568 \times 10^{-7}T^2 - 0.04278T + 12.3822 \text{ (J/g °C)} \]

The R² value was greater than 0.98. The average heat capacity of liquid SYSU-C4 is 1.19 J/g K.

The calculated heat capacity data for solid SYSU-C4 is very close to the sum of pure salts’ heat capacity from literature between 200°C and 600°C. The heat capacity of liquid SYSU-C4 is bigger than that of the solid state because of disorder for ions in liquid state. The additional energy stored inside the liquid state salt contributes to the increase part of heat capacity comparing solid state salt. When the temperature over 600°C, the value of heat capacity for the salt increases quickly because of the volatilization of the molten salt under N₂ current and it is distortion in measuring condition.

3.3. Density

The density of SYSU-C4 as function of temperature was plotted in Fig.5, where it was compared with the available data for Solar Salt and HTS [1,2]. It is observed that the density of SYSU-C4 linearly decreases from 2.555 g/cm³ to 1.91 g/cm³ with increasing temperature between 500°C and 750°C, which could be satisfactorily expressed by the equation:

\[ \rho (\text{g/cm}^3) = 4.02057 - 0.0027697T(\text{°C}) \] \hspace{1cm} (500-750°C)

The R² value of this equation was greater than 0.97. The density of SYSU-C4 was bigger than that of the Solar Salt and HTS in respective operating temperature range, which means that SYSU-C4 had a smaller thermal expansion when it was heated. So the cost of the thermal storage can be reduced.

3.4. Viscosity

The measured viscosity data of SYSU-C4 was given in Fig.6. It is showed that the viscosity of SYSU-C4 decreases from 4.0 cp to 3.0 cp with increasing temperature between 450°C and 600°C and the data can be fitted to a linear equation (R² was greater than 0.95):

\[ \mu (\text{cp}) = 7.1824 - 0.006797T(\text{°C}) \] \hspace{1cm} (450°C-600°C)

The stable variation as function of temperature allows the extrapolation of viscosity at even high temperature and the extrapolated viscosity at 650°C and 700°C was given in Fig.6. In the operating temperature range the viscosity of SYSU-C4 decreases to a relatively low value, which was suitable for the flow in the pipe.

3.5. Thermal stability

Thermal stability which determined how long the molten salt can be used is also an important property. The previous work [3] reported that the thermal stability of this ternary molten salt was not
good under open air condition, which was mainly attributed to the reactions between MgCl₂ and moisture come from atmosphere. In order to test the thermal stability of SYSU-C4 under real operation condition and reduce the influence of moisture and purge stream, about 40g SYSU-C4 were put into alumina crucible with a lid. The mass loss curves of SYSU-C4 under isothermal conditions after 18h are given in Fig.7. It was obviously that the mass loss of SYSU-C4 accelerated with the augment of temperature. After 18h, less than 1% of SYSU-C4 were lost below 600°C and less than 3% were lost below 700°C, which showed much better stability than in the open air condition. The negligible mass loss was mainly attributed to the volatilization of molten salts [10]. In a word, the total weight loss at 700°C is still acceptable for the realistic utility of the ternary eutectic salt mixture as a potential candidate for solar thermal energy storage applications.

![Graph 1](image1)

**Fig. 6. Viscosities of SYSU-C4 as function of temperature**

![Graph 2](image2)

**Fig. 7. Mass loss curves of SYSU-C4 under isothermal conditions**

4. Conclusions

DSC technology was used to identify the true eutectic point of ternary chloride salt mixture and the result revealed that was very perfect combination with theoretical calculation. Besides, all of the relevant thermal-physical properties of the ternary molten salt (named SYSU-C4) were determined. The heat capacity of SYSU-C4 was close to the literature data. The experimental density and viscosity all presented liner decreasing variation trend as function of temperature. The mass change curves showed that SYSU-C4 had a good thermal stability below 700°C. So, appropriate operating temperature, large heat capacity, low viscosity and good thermal stability all indicated that SYSU-C4 was suitable for heat transfer-thermal storage material.

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References