Properties and heat transfer coefficients of four molten-salt high temperature heat transfer fluid candidates for concentrating solar power plants

T L Liu[1], W R Liu[1] and X H Xu[1,2]

[1]School of Mechanical Engineering and Automation, Harbin Institute of Technology, (Shenzhen), Shenzhen 518055, Guangdong Province, China

E-mail: xuxinhai@hit.edu.cn

Abstract. Heat transfer fluid is one critical component for transferring and storing heat energy in concentrating solar power systems. Molten-salt mixtures can be used as high temperature heat transfer fluids because of their thermophysical properties. This paper studied the thermophysical properties of Li_2CO_3-Na_2CO_3-K_2CO_3 eutectic salt and three eutectic chloride salts NaCl-KCl-ZnCl$_2$ with different compositions in the range of 450-600ºC and 250-800ºC, respectively. Properties including specific heat capacity, thermal conductivity, density and viscosity were determined based on imperial correlations and compared at different operating temperatures. The heat transfer coefficients of using different eutectic salts as heat transfer fluids were also calculated and compared in their operating temperature range. It is concluded that all the four eutectic salts can satisfy the requirements of a high-temperature heat transfer fluid.

1. Introduction

Our society is facing with two major challenges: power shortage and environmental pollution. It is an urgent task for human beings to study renewable and sustainable energy. Concentrating solar power (CSP) has aroused many researchers' interests due to its potential to meet basic load applications, especially for applications with a large power output higher than 100 MW [1,2]. There are four most commonly used technologies in a CSP system: linear Fresnel reflector (LFR), solar power tower (SPT), parabolic trough collector (PTC), and parabolic dish system (PDS) [3]. Among these, less than 18% of the CSP plants utilize SPT, LFR and PDS, others utilize PTC to collect the solar energy. However, the most advanced CSP plants are the SPT-based plants, because they are more suitable for achieving very high temperature compared to other CSP plants and thereby can enhance the efficiency of converting heat into electricity [1,4]. A typical CSP plant consists of four major components: the solar collection system, the receiver, the heat transfer fluid (HTF) system and the traditional power block. The sunrays are concentrated onto the receiver by the reflector configuration in the solar collection system. The receiver absorbs the solar energy and transmits it to a HTF. The HTF acts as the thermal energy carrier transferring the concentrated heat to the power block which converts the heat into electricity [5].

HTF is one of the most important components in a CSP plant [5]. Due to the characteristics of low vapor pressure, high heat capacity, and excellent thermal stability, molten-salt mixtures have been widely used as HTF candidates for high temperature (higher than 500ºC) applications [6-10]. Operating a CSP plant requires a large quantity of HTF, so that it is important to select the most

appropriate HTF to minimize the cost and at the same time maximizing its performance [3]. The U.S. Department of Energy has funded for developing a new high-temperature HTF with a working temperature of at least 800ºC by using eutectic molten salts [11]. Other important requirements for the thermophysical properties of the HTF include: vapor pressure below 1.0 atm at 800ºC, specific heat capacity ≥1.5 kJ/(kg·K), thermal conductivity ≥0.51 W/(m·K), density ≤5400 kg/m^3, viscosity ≤0.012 Pa·s at 300ºC and ≤0.004 Pa·s at 600ºC.

The ability to exchange heat is one important characteristic of the HTF, which can be represented by the heat transfer coefficient h. In a theoretical study, h can only be determined based on its correlation with Nusselt number. The main objective of this paper is to compare the thermophysical properties and heat transfer coefficients of four eutectic molten-salt mixtures which could be used in CSP plants as high temperature HTFs. All the four kinds of molten-salt mixtures which include Li_2CO_3-Na_2CO_3-K_2CO_3 salts and three $NaCl$-KCl-$ZnCl_2$ salts with different composition ratios have thermally stable points higher than 650ºC. The innovation points of this paper are the calculation and comparison of heat transfer coefficient h for these eutectic molten salts. In section 2, equations to calculate the specific heat capacity, thermal conductivity, density and viscosity of the four molten salts were presented. In section 3, the importance of the heat transfer coefficient h and the methodology employed to calculate the heat transfer coefficient h based on Nusselt number was discussed. In section 4, the thermophysical properties and heat transfer coefficients of the four molten-salt mixtures at different operating temperatures were compared.

2. Thermophysical properties

In this study, four different eutectic molten-salt mixtures are considered, including one carbonate salts [12] and three chloride salts [13]. Compositions and thermophysical properties of them are listed in tables 1 and 2. They are all potential HTF candidates for a CSP tower power operating in the temperature above 550ºC because their thermal stability temperatures are all higher than 600ºC. Vignarooban *et al* [3] summarized the currently available molten-salt HTF candidates in a recent review, and the selected four eutectic molten salts are the only candidates which satisfy the thermal stability requirement.

Table 1. Compositions, melting points and stability points of heat transfer fluids.

	Carbonate Salts[a]	Chloride salts[b]		
Compositions	Li_2CO_3-Na_2CO_3-K_2CO_3	$NaCl$-KCl-$ZnCl_2$		
wt. %	32.1-33.4-34.5	7.5-23.9-68.6	8.1-31.3-60.6	10.0-15.1-74.9
Melting point (ºC)	400	204	229	213
Stability point (ºC)	658	> 800	> 800	> 800

[a] [12,14,15]
[b] [13]

Table 2. Heat transfer fluids' thermophysical properties.

Properties	Units	Temperature range (ºC)
Li_2CO_3-Na_2CO_3-K_2CO_3[a]		
$C_p = 1.61 \pm 0.08$	J/(g·K)	450 - 600
$\lambda = C_p \cdot \rho \cdot \alpha$	W/(m·K)	450 - 600
$\rho = 2.27 - 4.34 \times 10^{-4}T$	g/cm^3	450 - 600
$\mu = 0.0852\exp(\dfrac{3.51 \times 10^4}{RT})$	mPa·s	450 - 650

NaCl-KCl-ZnCl$_2$[b]

$C_p = 0.9 - 0.92$	J/(g·K)	230 - 350
$\lambda = 0.5145 - 2.3309 \times 10^{-4}T$	W/(m·K)	300 - 800
$\rho = 2.8783 - 0.9263 \times 10^{-3}T$	g/cm^3	300 - 800
$\mu = [0.12055 \exp(\frac{-T}{204.70939}) + 497613.0848 \exp(\frac{-T}{29.9196})] \times 10^3 + 3.41$	mPa·s	250 - 800

NaCl-KCl-ZnCl$_2$[b]

$C_p = 0.9 - 0.92$	J/(g·K)	230 - 350
$\lambda = 0.4372 - 1.2301 \times 10^{-4}T$	W/(m·K)	300 - 800
$\rho = 2.5417 - 0.5302 \times 10^{-3}T$	g/cm^3	300 - 800
$\mu = [152.3679 \exp(\frac{-T}{56.03143}) + 0.05994 \exp(\frac{-T}{235.78682})] \times 10^3 + 2.97$	mPa·s	250 - 800

NaCl-KCl-ZnCl$_2$[b]

$C_p = 0.9 - 0.92$	J/(g·K)	230 - 350
$\lambda = 0.3895 - 8.1686 \times 10^{-5}T$	W/(m·K)	300 - 800
$\rho = 2.5811 - 0.4321 \times 10^{-3}T$	g/cm^3	300 - 800
$\mu = 131.0731 \exp(\frac{-T}{62.36328}) \times 10^3 + 4.46$	mPa·s	250 - 800

[a] [12,14,15]
[b] [13]

The ternary LiNaK carbonate salts (Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$, 32.1-33.4-34.5 wt.%) has a melting point of 400ºC and a thermal stability temperature of 658ºC. An *et al* [错误!未定义书签。] studied the thermal conductivity, viscosity and density of the ternary LiNaK carbonate salts. Ejima *et al* also examined the viscosity of this eutectic salt mixture.

Li *et al* [16] proposed to use the NaCl-KCl-ZnCl$_2$ ternary salt mixture to replace the commercial nitrate based salts as high temperature HTFs. Three composition ratios of the NaCl-KCl-ZnCl$_2$ were founded to form eutectic mixtures and the thermophysical properties were all studied [13]. For the sake of convenient reference, this study used salt #1, salt #2 and salt #3 to denote the NaCl-KCl-ZnCl$_2$ salt mixtures with mass fraction ratios of 7.5%-23.9%-68.6%, 8.1%-31.3%-60.6%, and 10.0%-15.1%-74.9%, respectively. The working temperature ranges of the three chloride salt mixtures are from 250ºC to at least 800ºC.

3. Heat transfer coefficient calculation
The convection heat transfer coefficient *h* is expressed as,

$$h = -\lambda \frac{\left(dT_f / dy\right)_w}{T_w - T_b} \tag{1}$$

Where T_b is the fluid temperature, T_w is the wall temperature, λ is the thermal conductivity and $(dT_f/dy)_w$ is the fluid temperature gradient [5]. To have a high CSP plant's efficiency, the heat flux exchanged between the tube wall and the HTF must be high. The heat flux can be increased by increasing the heat transfer coefficient or increasing the temperature difference between the fluid and the wall. However, molten salts could decompose or vaporize at too high temperatures, so the

temperature difference between the fluid and the wall is limited if using molten salts as HTFs. Therefore, the heat transfer coefficient h is critical. Equation (1) shows that the heat transfer coefficient h can be improved by two methods: increasing the thermal conductivity λ or the temperature gradient $(dT_f/dy)_w$. For a given HTF, the thermal conductivity λ is directly related to the HTF, and the temperature gradient $(dT_f/dy)_w$ can only be increased by increasing the velocity of the flowing HTF inside the tube. However, high velocity results in a high pumping power loss. To reach a maximized heat transfer performance for a specific HTF, a trade-off is necessary between these two effects [5].

In practice, h is calculated by the Nusselt number Nu,

$$h = \frac{Nu\lambda}{d} \tag{2}$$

Where d is the characteristic length, and λ is the fluid thermal conductivity.

Generally the imperial equation proposed by Wu *et al* [17] can be used to determine the Nusselt number for the molten-salt HTFs, which is shown in equation (3).

$$Nu = 0.02948\,Re^{0.787}\,Pr^{1/3} \tag{3}$$

Which is valid for $10^4 \leq Re \leq 4.6 \times 10^4$, $1.6 \leq Pr \leq 23.9$. Re and Pr are calculated as,

$$Re = \frac{\rho VD}{\mu} \tag{4}$$

$$Pr = \frac{C_p\mu}{\lambda} \tag{5}$$

Where ρ is the density, V is the fluid velocity, D is the characteristic length, C_p is the specific heat capacity, μ is the dynamic viscosity and λ is the thermal conductivity.

The usual tube size of 25 cm internal diameter was selected, and the selected fluid velocity is 2 m/s for the HTFs [5].

4. Results and discussion

4.1. The comparison of specific heat capacity C_p

The specific heat capacity of the Li_2CO_3-Na_2CO_3-K_2CO_3 molten-salt mixture can be taken as a constant of 1.61 J/(g·K) at the temperature range of 450°C to 600°C [12]. The heat capacities of the three eutectic chloride salts were measured in the temperature range from 230°C to 350°C. In this temperature range, the heat capacities varying between 0.9 and 0.92 J/(g·K) did not show appreciable change with temperature, and thus constant heat capacities can be assumed for engineering applications [13]. It is noticed that the heat capacity of Li_2CO_3-Na_2CO_3-K_2CO_3 is 43.5% larger than those of the $NaCl$-KCl-$ZnCl_2$ systems. The larger heat capacity of the Li_2CO_3-Na_2CO_3-K_2CO_3 compared to that of the chloride salt system demonstrates that the carbonate salts have better energy storage capacity.

4.2. The comparison of thermal conductivity λ

Thermal conductivity of a heat transfer fluid determines the thermal energy transfer efficiency and thus is considered as a significant parameter for practical applications [18]. The thermal conductivities of the Li_2CO_3-Na_2CO_3-K_2CO_3 eutectic salt mixture are 0.454, 0.458, 0.470 and 0.492 W/(m·K) at 450, 500, 550, and 600°C, respectively. It slightly increases with increasing temperature. The thermal conductivities of the $NaCl$-KCl-$ZnCl_2$ systems were measured at temperatures between 300°C and 800°C. Figure 1 shows that the thermal conductivities of all the three eutectic salts are in the range of 0.26-0.38 W/(m·K) and they all slightly decrease with increasing temperature. The thermal

conductivity of Li_2CO_3-Na_2CO_3-K_2CO_3 is higher than those of NaCl-KCl-$ZnCl_2$, indicating that the LiNaK carbonate salt can transfer and store energy in a more efficient way.
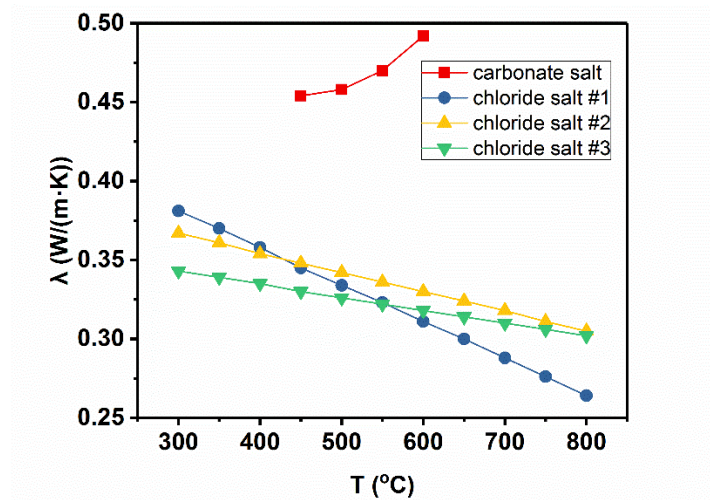

Figure 1. Thermal conductivity of the four molten salts as function of temperature.

4.3. The comparison of density ρ
Figure 2 shows comparison of densities at the temperature between 300 and 800ºC. All the densities linearly decrease with increasing temperature. The density of LiNaK carbonate salt is in the range of 1.9-2.0 g/cm^3 and the three eutectic chloride salts is in the range of 1.9-2.3 g/cm^3. Because of the relatively higher density of $ZnCl_2$, the salt with a higher fraction of $ZnCl_2$ has higher density.
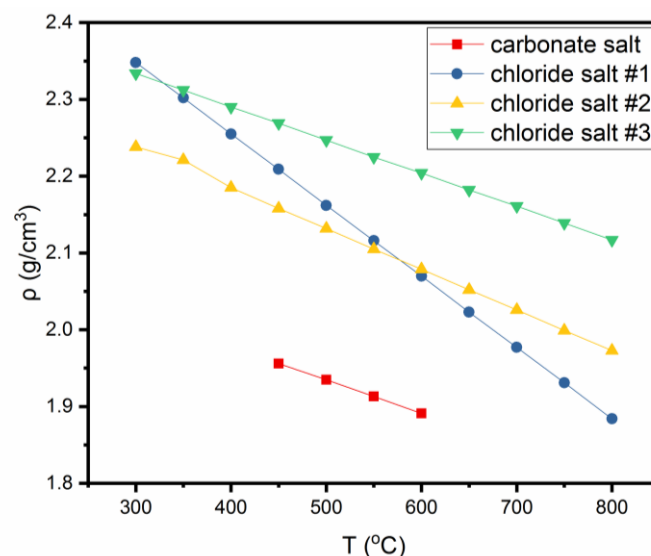

Figure 2. Density of the four molten salts as function of temperature.

4.4. The comparison of viscosity μ
The viscosity of the Li_2CO_3-Na_2CO_3-K_2CO_3 exponentially decreases as the temperature increases. The viscosities of the NaCl-KCl-$ZnCl_2$ mixtures were measured in the temperature range from 250ºC to 800ºC. Figure 3 shows comparison of the viscosities. The results show that the viscosity of the LiNaK carbonate salt is significantly higher than those of the chloride salt mixtures in its operating temperature range. As for the chloride salt mixtures, their viscosities are quite low at relatively high

temperature above 400ºC. The viscosities are around 15, 7 and 4 mPa·s for the chloride salt mixtures at 300, 400 and 700ºC, respectively. It can be seen that the low mass fraction of $ZnCl_2$ in salt #2 contributes to its low viscosity. However, the differences in the viscosities of the three eutectic molten salts are trivial.
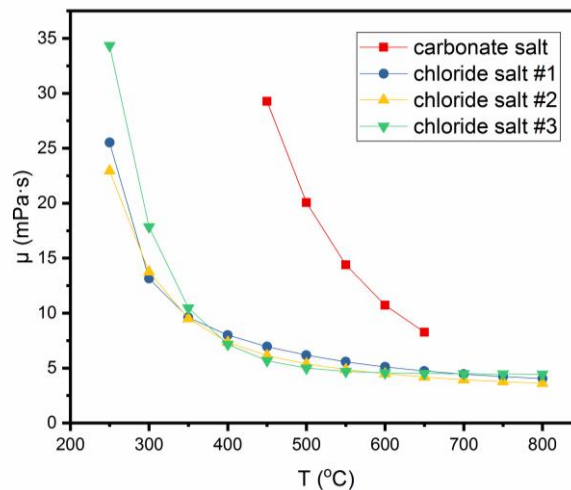

Figure 3. Viscosity of the four molten salts as function of temperature.

4.5. The comparison of heat transfer coefficient h

Figure 4 plots the heat transfer coefficients of the four molten salts as functions of temperature. For LiNaK carbonate salt, *h* increases from 1640 to 2520 W/(m^2·K) as its working temperature increases from 450ºC to 600ºC. For chloride salt #1, *h* ranges between 1800 and 2210 W/(m^2·K). It increases with *T* up to a maximum value at 550ºC and then decreases. For salt #2 and salt #3, *h* ranges between 1680 and 2500 W/(m^2·K) and between 1470 and 2490 W/(m^2·K), respectively. The maximum heat transfer coefficient value is reached at 700ºC and 550ºC, respectively. The trend of the heat transfer coefficients of the chloride salts are mainly due to that the thermal conductivity decreases with increasing temperature.
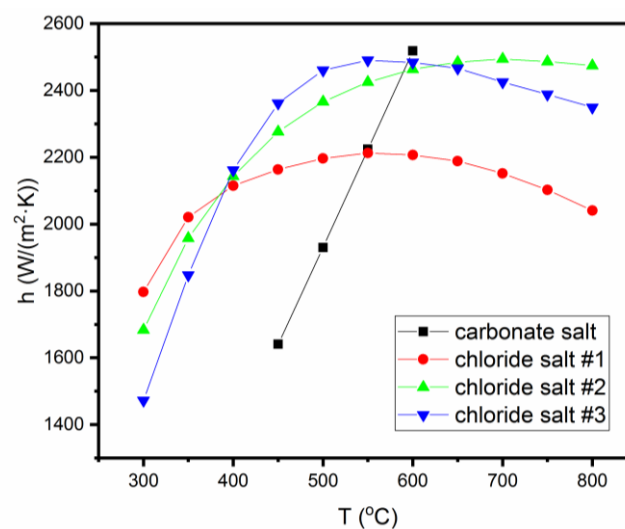

Figure 4. Heat transfer coefficient of the four molten salts as function of temperature.

5. Conclusion

In this paper, the thermophysical properties of the LiNaK carbonate salt and three chloride salts were compared. The specific heat capacity C_p can be regarded as constants for all the salts at their separate operating temperature ranges. However, C_p of the LiNaK carbonate salt is larger than those of the three chloride salts. The thermal conductivity λ of the LiNaK carbonate salt slightly increases with increasing temperature. In the contrary, λ slightly decreases with increasing temperature of the three chloride salts. Besides, it is lower than that of the LiNaK carbonate salt. All the densities linearly decrease with increasing temperature. Densities of the three chloride salts are slightly higher than that of the LiNaK carbonate salt. In addition, density of the chloride salt #3 is slightly higher than those of the other chloride salts due to a higher fraction of $ZnCl_2$ in its compositions. All the viscosities of the four eutectic salts exponentially decrease as the temperature increases. However, the viscosity μ of the LiNaK carbonate salt is significantly higher than that of the three chloride salts in its operating temperature range. For the convection heat transfer coefficient h, the chloride salts generally have higher h than the carbonate salts. In the temperature range of 400 – 600ºC, chloride salts #3 has the highest heat transfer coefficient. While the temperature is over 600ºC, the heat transfer coefficient of chloride salts #2 has the maximum value.

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