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Review

Survey of Properties of Key Single and Mixture Halide Salts for Potential Application as High Temperature Heat Transfer Fluids for Concentrated Solar Thermal Power Systems

Chao-Jen Li [1, 2], Peiwen Li [1,*], Kai Wang [1], Edgar Emir Molina [1]

[1] Department of Aerospace and Mechanical Engineering, The University of Arizona, Tucson, AZ 85721, USA

[2] Visiting Researcher, on leave from Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan 31040, R.O.C.

* **Correspondence:** Email: peiwen@email.arizona.edu; Tel: +1-520-626-7789; Fax: +1-520-621-8191.

Abstract: In order to obtain high energy efficiency in a concentrated solar thermal power plant, more and more high concentration ratio to solar radiation are applied to collect high temperature thermal energy in modern solar power technologies. This incurs the need of a heat transfer fluid being able to work at more and more high temperatures to carry the heat from solar concentrators to a power plant. To develop the third generation heat transfer fluids targeting at a high working temperature at least 800 ^{o}C, a research team from University of Arizona, Georgia Institute of Technology, and Arizona State University proposed to use eutectic halide salts mixtures in order to obtain the desired properties of low melting point, low vapor pressure, great stability at temperatures at least 800 ^{o}C, low corrosion, and favorable thermal and transport properties. In this paper, a survey of the available thermal and transport properties of single and eutectic mixture of several key halide salts is conducted, providing information of great significance to researchers for heat transfer fluid development.

Keywords: CSP; Heat transfer fluid; Molten salts; Ionic and covalent halide salts; Properties

1. Introduction

The use of various sources of renewable energy becomes increasingly important in the worldwide effort of ameliorating problems associated with the use of fossil fuels. No doubt that solar

energy is one of the most attractive sources of clean energy. Among different solar energy technologies, concentrated solar thermal power (CSP) is believed to be very promising for large-capacity power generation. Due to the possibility of incorporating solar thermal storage into the power generation system, CSP can better meet the power demand at the time sun is down [1-4].

In the past decade we have seen a worldwide significant increase in solar thermal power generation capacity with the combination of solar thermal storage. The number of solar thermal power plants constructed in Southern Europe, USA, Africa, and Australia is increasing, which generate electricity by replacing conventional fuel-combustion facilities in power plants with solar thermal collection devices. Solar concentrators collect thermal energy and raise the temperature of the heat transfer fluid (HTF), which is fed to a heat exchanger and boils water into steam of high temperature and high pressure. The steam subsequently drives steam turbines, which generate electricity. There are four types of solar concentration technologies, parabolic trough, solar power tower, Fresnel reflectors, and solar dish Stirling engines. The first three use a HTF to take away the heat from the collectors and use the heat in power generation systems.

Heat transfer and heat storage are the two important roles of a HTF in concentrated solar power systems. The well-known HTF used in CSP systems in the earlier stage is made of organic substances, which is an eutectic mixture of biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$), sold under the brand name of Therminol VP-1 and Dowtherm A [5,6]. It exhibits a low melting point of 12 °C (285 K) but is limited to an upper temperature of 390 °C (673 K) due to chemical dissociation above this temperature. This is not sufficiently high for the increasing demand of thermal efficiency of a CSP system. The high vapor pressure (10 atm at 390 °C) and high cost of this HTF also significantly restrict its application.

Increasing the high temperature in a CSP plant from 390 ^{o}C to 500 ^{o}C (using molten salts) would increase the Rankine cycle efficiency to the 40% range (compared to the efficiency of 37.6% using Therminol VP-1) and thereby reducing the levelized electricity cost by 2 cents/kWh [7,8]. For more development of CSP technologies, finding a heat transfer fluid working at much high temperatures is important.

There are multiple demands if a fluid serves as a heat transfer fluid in a large range of temperature variation. First the fluid should have a low freezing point to avoid solidification in the circulation system. Second, the fluid should be chemically stable at a high temperature, and at the same time to have low vapor pressures (below 1.0 atm) due to the safety requirement of containers and pipes. Third, the fluid must have minimum corrosion to the metal pipes and containers that hold the fluids. Forth, the heat transfer fluid should have favorable transport properties (low viscosity and high thermal conductivity) for efficient heat exchange and low pressure loss in the flow and circulation.

Molten salts have been studied for their possibility of high working temperatures, and in the meantime with low melting points, moderate density, high heat capacity, and high thermal conductivity. Other than favorable thermal and transport properties, long term thermal stability (or chemical stability with less corrosion to containers) and low cost of molten salt HTF is also very critical [9-12].

Due to the very strong demand, the research work for suitable molten salts for HTFs as well as thermal energy storage materials in solar thermal power plants [13,14] is very active recently. The studies on some inorganic salts used for thermal energy storage materials are available in several papers [15-19]. Zalba et al. [16] summarized thermal characteristics of some phase-change materials.

Kenisarin [17] and Gil et al. [18,19] analyzed some phase change materials and the practical applications for solar thermal storage. So far, several well-recognized commercial molten salts by eutectic mixtures of nitrates or nitrites have been used in concentrated solar power systems mainly for thermal storage purpose, but can also be used as HTF. A binary mixture, Solar Salt (60 wt.% $NaNO_3$/ 40 wt.% KNO_3) has been used as thermal storage material in the 10 MWe solar-II central receiver project in California [20-22], in the 2-tank direct system of the Archimede project in Italy [23], and the indirect thermal energy storage system for the Andasol plant in Spain [24,25]. Solar Salt has a thermal stability (below 600 ^oC) and a relatively high melting point (220 ^oC). A new heat transfer fluid called Hitec, which is a ternary salt mixture of 53 wt.% KNO_3/ 7 wt.% $NaNO_3$/ 40 wt.% $NaNO_2$, has been considered to replace the Solar Salt because of its low freezing point of 142 ^oC [26]. Hitec is thermally stable at temperatures up to 454 ^oC, and may be used at temperature up to 538 ^oC for a short period [27]. A modified version, Hitec XL, is a mixture of 48 wt.% $Ca(NO_3)_2$/ 7 wt.% $NaNO_3$/ 45 wt.% KNO_3 which melts at about 133 ^oC and may be used at a temperature up to 500 ^oC [28-43]. Different compositions of $Ca(NO_3)_2$/ $NaNO_3$/ KNO_3 have been identified in the open literature as eutectic salts [29-43]. The ternary eutectic salt with composition of 44 wt.% $Ca(NO_3)_2$/ 12 wt.% $NaNO_3$/ 44 wt.% KNO_3 melts at 127.6 ^oC and its thermal stability is good at up to 622 ^oC [43]. Different phase diagrams also have been published for the $Ca(NO_3)_2$/ $NaNO_3$/ KNO_3 system [44-47].

There are also other ternary salts being developed and undergoing tests for industrial application. The eutectic salt in composition of 25.9 wt.% $LiNO_3$/ 20.0 wt.% $NaNO_3$/ 54.1 wt.% KNO_3 melts at about 118 ^oC and thermal stability is up to 435 ^oC [48,49]. The salt in composition of 30 wt.% $LiNO_3$/ 18 wt.% $NaNO_3$/ 52 wt.% KNO_3 is reported to have thermal stabilities up to 550 ^oC and melting point of 120 ^oC [50-52]. Another ternary nitrate salt mixtures consisting of 50–80 wt.% KNO_3/ 0–25 wt.% $LiNO_3$/ 10–45 wt.% $Ca(NO_3)_2$ melts below 100 ^oC and thermal stability is up to 500 ^oC [53]. Sandia National Laboratories developed a low-melting heat transfer fluid made of a mixture of four inorganic nitrate salts: 9–18 wt.%$NaNO_3$/ 40–52 wt.%KNO_3/ 13–21 wt.%$LiNO_3$/

Table 1. Summary of the key data of some heat transfer fluids.

Name	Formula	T_{melt} (^oC)	T_{max}(^oC)
Therminal VP-1	($C_{12}H_{10}$) and ($C_{12}H_{10}O$). Percentage not know.	12	390
Solar Salt	wt. 60% $NaNO_3$ /40% KNO_3	220	600
Hitec	wt. 53% KNO_3/7% $NaNO_3$/40% $NaNO_2$	142	454–538
Hitec XL	wt. 48% $Ca(NO_3)_2$/7% $NaNO_3$/45% KNO_3	133	500
NS-1	wt. 44% $Ca(NO_3)_2$/12% $NaNO_3$/44% KNO_3	127.6	622
NS-2	wt. 25.9% $LiNO_3$/20.0% $NaNO_3$/54.1% KNO_3	118	435
NS-3	wt. 30% $LiNO_3$/18% $NaNO_3$/52% KNO_3	120	550
NS-4	wt. 50-80% KNO_3/0-25% $LiNO_3$/10-45% $Ca(NO_3)_2$	100	500
NS-5	wt. 17.77% $LiNO_3$/15.28% $NaNO_3$/35.97% KNO_3/ 30.98% $2KNO_3 \cdot Mg(NO_3)_2$	100	
NS-6	wt. 17.5% $LiNO_3$/14.2% $NaNO_3$/50.5% KNO_3/ 17.8% $NaNO_2$	99	500
NS-7	wt. 6% $NaNO_3$/23% KNO_3/8% $LiNO_3$/ 19% $Ca(NO_3)_2$/44% $CsNO_3$	65	561

20–27 wt.% $Ca(NO_3)_2$ [54]. This quaternary salts mixture has a melting temperature less than 100 °C and the thermal stability limit is greater than 500 °C. The quaternary salt 17.77 wt.% $LiNO_3$/ 15.28 wt.% $NaNO_3$/ 35.97 wt.% KNO_3/ 30.98 wt.% $2KNO_3 \cdot Mg(NO_3)_2$ melts at about 100.9 °C but there is no data about thermal stability [55]. Another quaternary nitrate salt mixture consisting of 17.5 wt.% $LiNO_3$/ 14.2 wt.% $NaNO_3$/ 50.5 wt.% KNO_3/ 17.8 wt.% $NaNO_2$ has a melting point of 99 °C and thermal stability at up to 500 °C [56]. Eutectic mixture with five species of salts also has been developed, for example, the salt with compositions of 6 wt.% $NaNO_3$/ 23 wt.% KNO_3/ 8 wt.% $LiNO_3$/ 19 wt.% $Ca(NO_3)_2$/ 44 wt.% $CsNO_3$ melts at 65 °C and has thermal stability of up to 561 °C [29]. Nevertheless, nitrate and nitrite salt systems have been found not thermally stable at temperature above 600 °C from a large amount of research works. A summary of the above mentioned HTFs is in Table 1.

A target of high temperature at 800 °C for CSP has been proposed by US Department of Energy. This is possible to accomplish Brayton power cycle, which can further increase the heat-to-electricity efficiency. Therefore, it is proposed recently to replace molten nitrate-nitrite salt with other kinds of salts to possibly increase the applicable temperatures to the level of 800 °C and even up to 1000 °C. Hundreds of inorganic salts and salt composites for HTF and latent heat storage in the temperature ranging from 120 °C to 1000 °C are listed in Kenisarin's review paper [57]. Those materials are on the basis of chlorides, fluorides, bromides, hydroxides, nitrates, carbonates and other salts. He found out that almost no single inorganic salt possesses decent properties to serve as a qualified HTF. Binary and ternary eutectic compositions based on fluorides and chlorides are the most prospective materials in term of their possibly favorable thermal and transport properties, as well as reasonably low cost in particular.

The eutectics of fluoride salts have been utilized in space solar power and molten salt nuclear reactors because of their favorable thermal and transport properties, especially heat storage capacity, but with the disadvantage of high cost, material compatibility and toxicity [58-60]. Carbonates may also be used for high temperature HTF and latent heat storage materials, but with drawbacks of high viscosity and easy degradation [61,62]. Consequently, chlorides salts are attractive due to their possibly favorable properties and especially low cost [63].

Funded by U.S. Department of Energy, a team by researchers from the University of Arizona, Georgia Institute of Technology, and Arizona State University has been conducting studies to ternary, quaternary and even higher order eutectic salts based on five key species of halide salts—$AlCl_3$, $ZnCl_2$, $FeCl_3$, NaCl, and KCl. These species are relatively inexpensive and also have great amount of reserve on the earth. The mixing of these ionic and covalent salts is expected to create favorable properties needed for HTF.

It is understandable that ionic and covalent halide salts are different in molecule size, shape, and chemical bonding. The bonding of positive ion and negative ion can make disorder leading to eutectic mixture with low melting temperatures. In Figure 1, strong evidences of low melting points at some eutectic compositions are shown in the phase diagrams of some binary and ternary mixtures by halide ionic salt with covalent salt (NaCl-$AlCl_3$, KCl-$AlCl_3$, NaCl-$ZnCl_2$, KCl-$ZnCl_2$, NaCl-KCl-$AlCl_3$, NaCl-KCl-$ZnCl_2$). Although very promising, a significant amount of work needs to be conducted to fully understand all the properties of these salts mixtures.

Obviously, identifying the eutectic compositions that have low melting points is only the first step of developing a HTF. As the final goal, a HTF should meet the target of thermal and transport properties in a relatively wide temperature range from below 250 °C to at least above 800 °C. To

obtain the thermal and transport properties (vapor pressure, density, viscosity, specific heat, thermal conductivity) for a high order mixture (of ternary and quaternary components), the properties of all individual components as well as all the low-order salt mixtures have to be identified. For this purpose, the present paper reviews the currently available experimental data for density, viscosity,

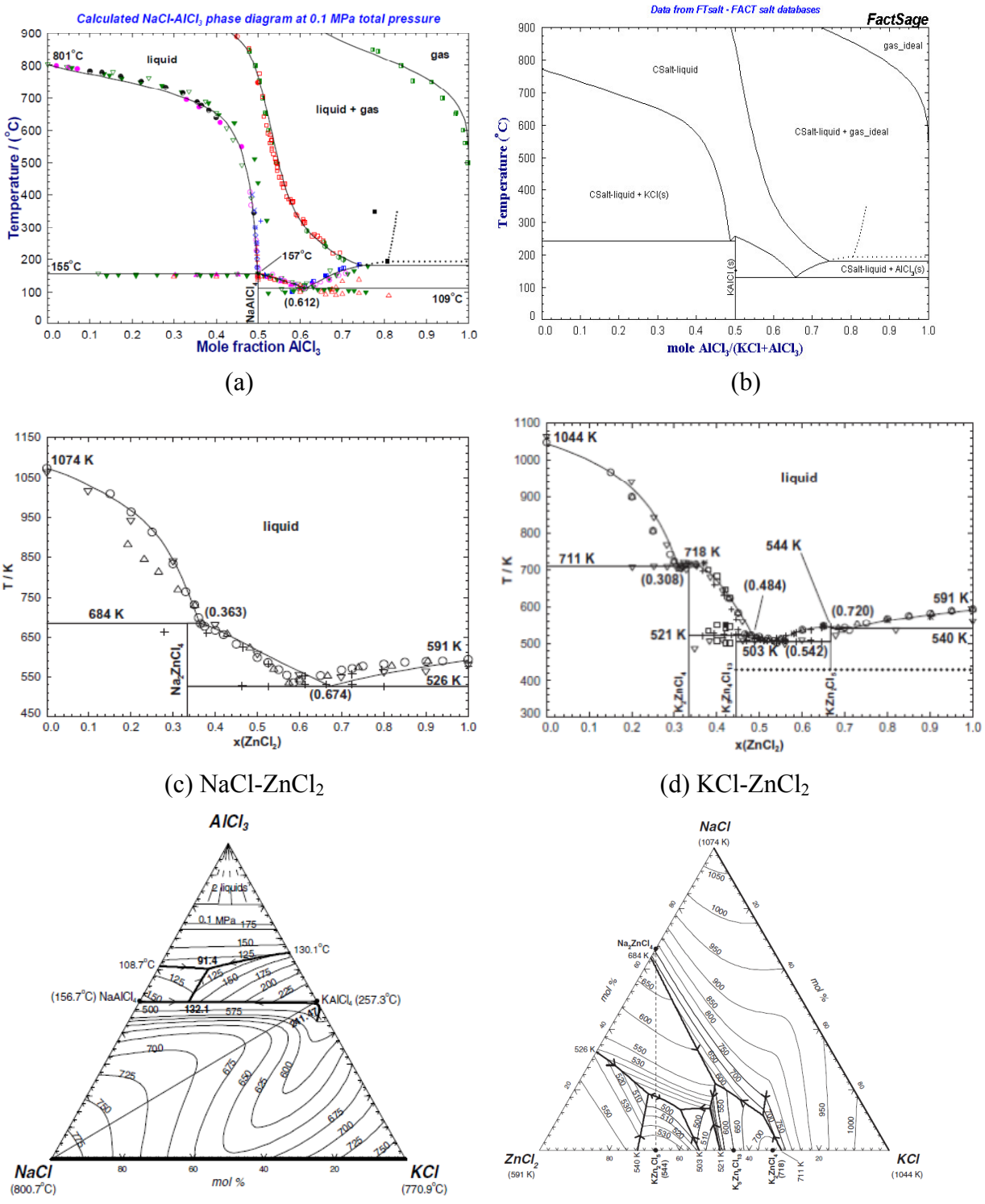


Figure 1. Phase diagrams of binary and ternary mixtures of ionic and covalent halide salts [64,65].

thermal conductivity, specific heat capacity, vapor pressure, and melting point of several halide salt single species as well as their binary to ternary mixtures. These data are expected to serve as the basis for further work of developing high order eutectic mixtures with understanding of their thermal and transport properties.

2. Properties of Several Popular Single Halide Salts in Molten State

In this section, the thermal and transport properties of the five single species of molten salt ($AlCl_3$, $ZnCl_2$, $FeCl_3$, NaCl, KCl) are provided for reference and evaluation on whether a salt can contribute to a better property of a possible eutectic salt mixture.

2.1.Aluminum chloride ($AlCl_3$)

This salt has a relatively low ***melting point*** which is T_m = 465 K (192 ^oC) [66]. However, it sublimes early at a temperature of 180 ^oC. The surveyed ***properties*** for molten $AlCl_3$ [66] are shown in Figure 2. The properties as functions of temperatures are given by the following equations:

$$\rho = 3.7660038 - 1.3346 \times 10^{-2} T + 2.7622 \times 10^{-5} T^2 - 2.2331268 \times 10^{-8} T^3 \quad (1)$$

where the units are ρ(g/cm^3), T (K) in the range of 465–560 K.

$$\mu = 3.2146 - 9.6606 \times 10^{-3} T + 7.4554 \times 10^{-6} T^2 \quad (2)$$

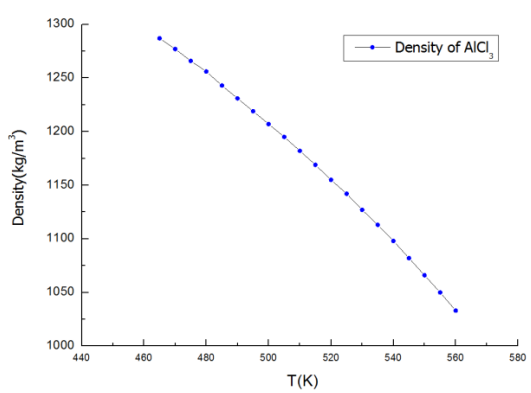
where the unit of viscosity is 10^{-3} (Pa s), and temperature is in K, in the range of 470–560K. The low viscosities may make $AlCl_3$ a very good component for a eutectic salt mixture as the low viscosity is important to a HTF.

$$P_{vap} = 10^{(7.42055 - 1948.55/T)} \quad (3)$$

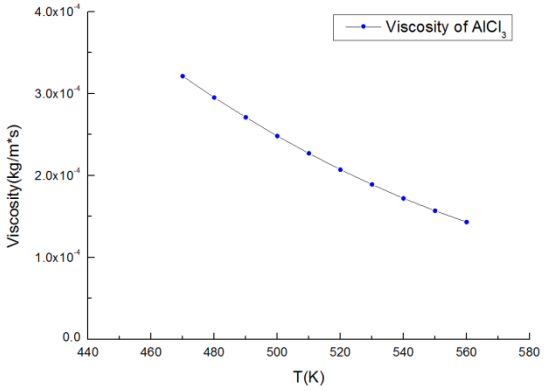
where the unit of pressure is P_{vap} (mm*Hg = 133.32 Pa), and the temperature is in K, in the range of 455–530K.

The ***specific heat capacity*** of liquid $AlCl_3$ does not change greatly in a wide range of temperatures from 466–1500K, which is around C_p = 125.5 J/mol*K or equivalent to 941.2 J/kg*K [67].

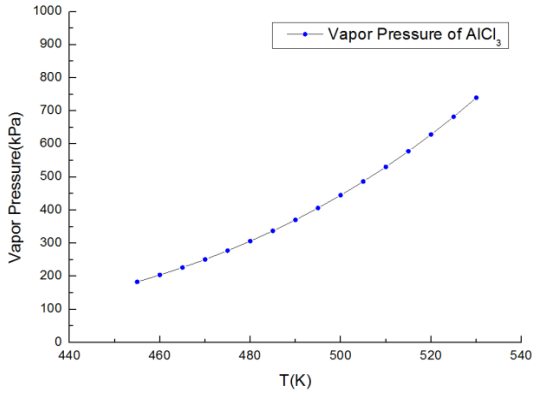
The ***vapor pressures*** of $AlCl_3$ are quite high which are not favorable as a heat transfer fluid. It is thus expected that ionic salts in a eutectic mixture with $AlCl_3$ can create inter-molecular bonding to suppress the vapor pressure. There are no thermal conductivity data found for liquid $AlCl_3$ in the current survey.



(a) Density [66].



(b) Viscosity [66].



(c) Vapor pressure [66].

Figure 2. Properties for molten salt $AlCl_3$ at different temperatures.

2.2. Zinc chloride ($ZnCl_2$)

Due to the low melting point and relatively low vapor pressure (compared to that of $AlCl_3$), $ZnCl_2$ is a very important species in halide salt family to contribute to a low melting point in a eutectic salt. The ***melting point*** of $ZnCl_2$ is T_m = 556 K (283 ^oC) [68]. Other properties are summarized as follows.

The ***density***, ***viscosity, and vapor pressure*** of molten $ZnCl_2$ versus temperatures are shown in Figure 3. The expressions for these properties as function of temperatures are given in Eqs. (4)-(6).

$$\rho = 2.424 - 0.00046 \times (T - 773) \tag{4}$$

where the units are ρ(g/cm^3), T (K), and the equations is applicable in a temperature range of 758.7–823.7 K.

$$\ln(\mu) = 0.2686 - 2665730.8 \times \ln(T)/T^2 + 19840539/T^2 \tag{5}$$

where μ is in cp or 10^{-3} Pa s, and T is in (K); the range of temperature is in 571–893K.

It is interesting to see from Figure 3(b) that the viscosity at low temperatures is high but it decreases dramatically when temperature increases. The low viscosity at high temperature is

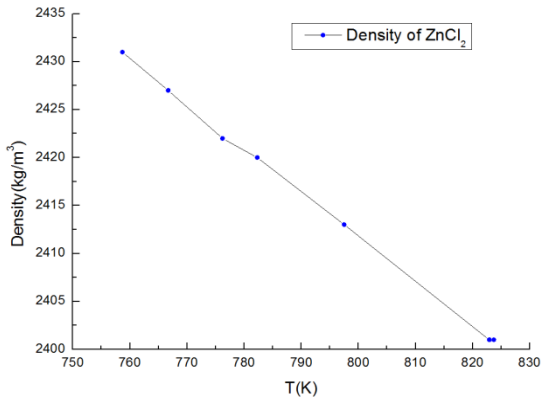
advantageous; while the high viscosity at low temperature should be modified by adding other components in a eutectic salt mixture.

The ***vapor pressure*** of liquid $ZnCl_2$ is relatively low compared to that of $AlCl_3$. As shown in Figure 3 (c) the vapor pressure of $ZnCl_2$ is quite low at temperatures below 600 ^oC, and at around 800 ^oC the vapor pressure reaches 2.0 atm. The correlation of vapor pressure and temperature reported by Keneshea and Cubicciotti [69] is in the form of

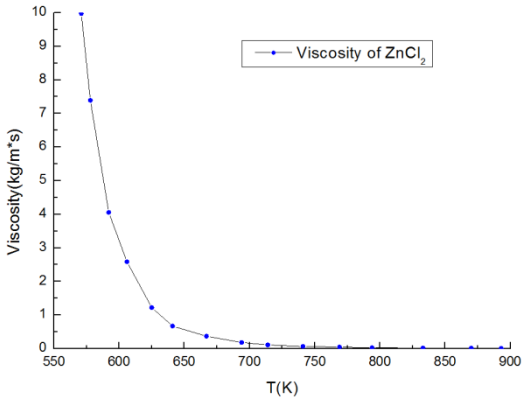
$$\log p(mmHg) = (-8415.2/T) - 5.034 \log T + 26.420 \quad (6)$$

where the unit of temperature is K, mm*Hg = 133.32 Pa. The relatively low vapor pressure of $ZnCl_2$ compared to that of $AlCl_3$ makes it a more favorable component to contribute to a relatively lower vapor pressure in a eutectic salt mixture.

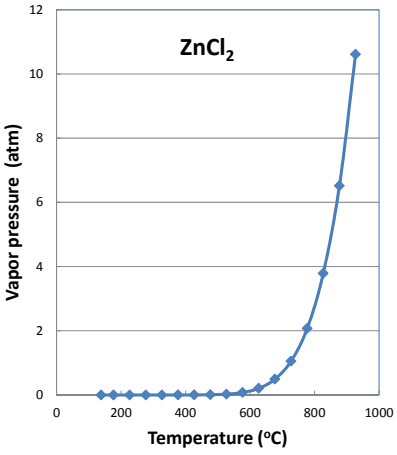
The ***specific heat capacity*** in the temperature range of 591–973K is around 24.1 cal/mol*K [70], or 739.54 J/(kg K). The present review could not find ***thermal conductivities*** for molten $ZnCl_2$.



3(a) Density[71]



3(b) Viscosity [72]



3(c) Vapor pressure [69]

Figure 3. Properties for molten salt $ZnCl_2$.

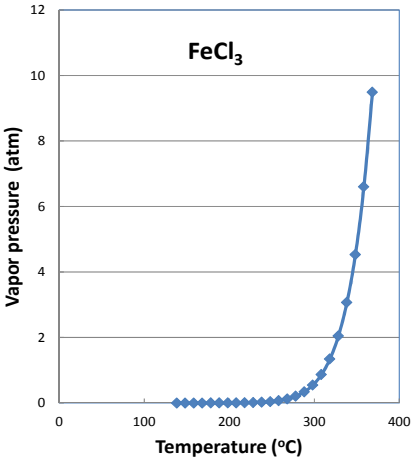


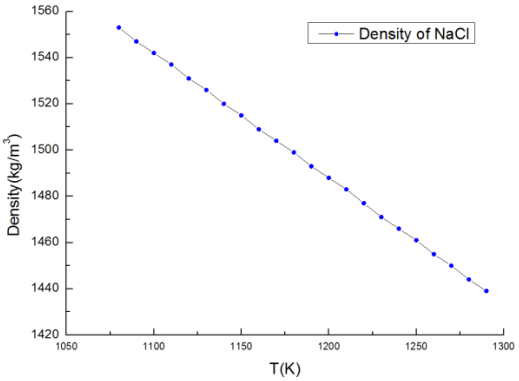
Figure. 4 Vapor pressure of liquid $FeCl_3$ [73].

2.3. Iron (III) chloride ($FeCl_3$)

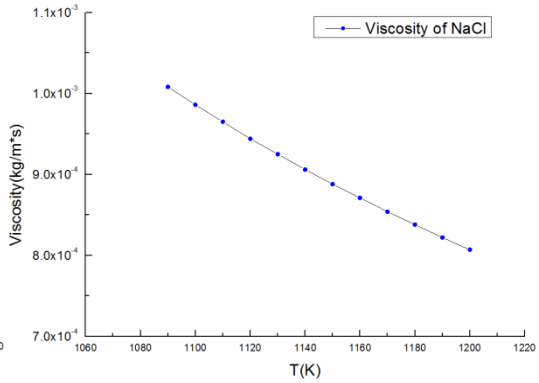
The ***melting point*** of salt $FeCl_3$ is T_m = 555 K (282 ^oC) [68]. The ***specific heat capacity*** of molten $FeCl_3$ is Cp = 133.89 J/mol*K or 825.43 J/kg*K in the temperature range of 577–1500 K. This salt has a rather high ***vapor pressure*** as shown above in Figure 4. At about 340 ^oC the vapor pressure already reaches 2 atm [73]. For this salt to be a component in a eutectic salt mixture, its high vapor pressure can be a problem of concern. No other properties were found for molten $FeCl_3$ in this survey.

2.4. Sodium chloride (NaCl)

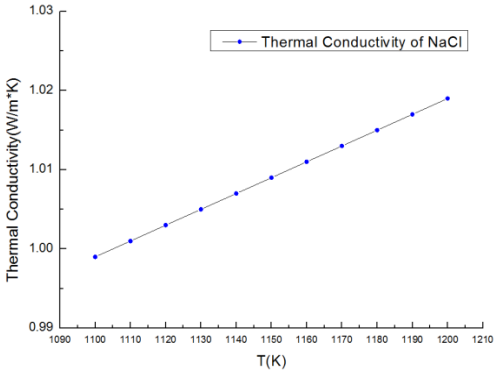
Well known as the table salt, NaCl has a ***melting point*** of T_m = 1075 K (802 ^oC) [66]. NaCl also has an almost unlimited reserve in seawater and thus has relatively low cost. Properties of molten NaCl are surveyed and given in Figure 5.



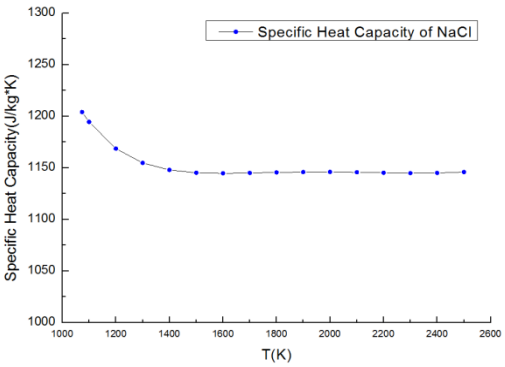
(a) Density [66]



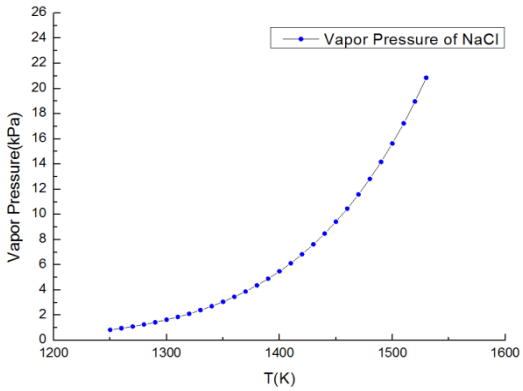
(b) Viscosity [66]



(c) Thermal conductivity [66]



(d) Specific heat capacity [66]



(e) Vapor pressure [66]

Figure 5. Properties of molten NaCl against temperatures.

The correlations of the properties were given in Eqs. (7) to (9). For density there is

$$\rho = 2.1393 - 5.430 \times 10^{-4} T \tag{7}$$

where the units are ρ(g/cm^3) and T(K). The equation is applicable in the range of temperature of 1080–1290 K.

The expression of viscosity is

$$\mu = 0.08931 \exp(5248.1/RT) \tag{8}$$

the unit of viscosity is μ(cp) and that of temperature is T(K), the range of temperatures for this equation is 1090–1200 K and the universal gas constant is R = 1.98716 (cal/K*mol). The relatively low viscosity of molten NaCl is favorable for it being used as a component in a eutectic salt mixture, which needs to have low viscosities at high temperatures.

The expression of thermal conductivity is

$$k = 1.868 \times 10^{-3} + 4.73 \times 10^{-7} T \tag{9}$$

where k has unit of (cal/cm*s*K = 418.4 W/m-K), and T is in (K), for the range of 1100–1200 K.

The expression of specific heat capacity is

$$C_p = -42.4478 + 113.526 \times t - 43.6466 \times t^2 + 5.89663 \times t^3 + 39.1386/t^2 \tag{10}$$

where unit of Cp is J/(mol*K), t = T(K)/1000, and T is in (K). The equation is applicable in a range of temperature from 1074 K to 2500 K.

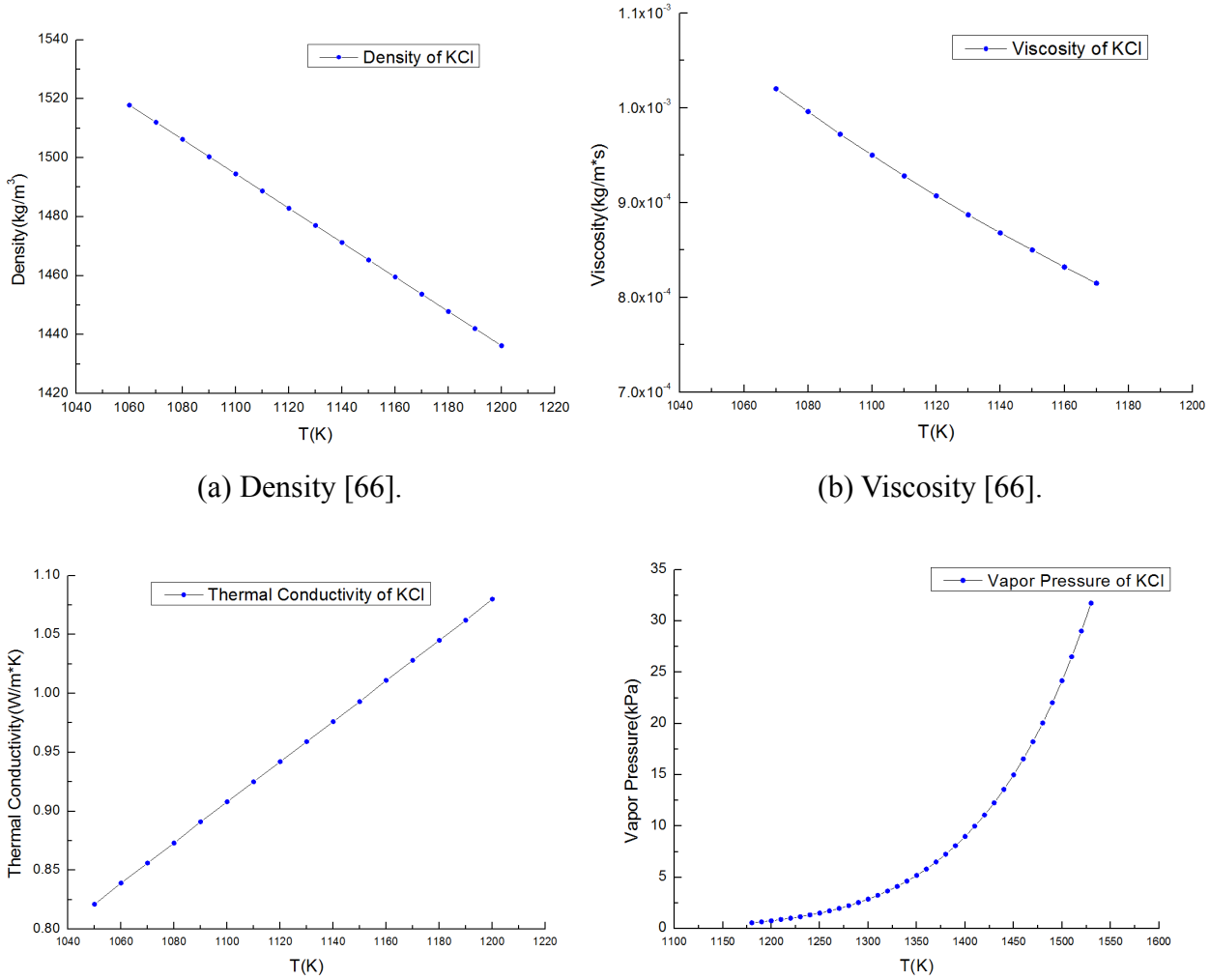
The vapor pressure in a narrow temperature range for molten NaCl is expressed as:

$$P_{vap} = 10^{(8.4459 - 9565/T)} \tag{11}$$

where P_{vap} is in (mm*Hg = 133.32Pa), T is in (K), and the range of the temperature for the equation is 1250–1530 K. The low vapor pressure of molten NaCl is very favorable for a heat transfer fluid.

2.5. Potassium chloride (KCl)

Potassium chloride has a ***melting point*** of T_m = 1043 K (770 ^oC) [66]. The properties surveyed for molten salt KCl are given in Figure 6. The corresponding expressions of the properties against temperatures for the curves are given in Eqs. (12) to (15).



(a) Density [66]. (b) Viscosity [66].

(c) Thermal conductivity [66]. (d) Vapor Pressure [66].

Figure 6. Properties of molten KCl against temperatures.

For density, there is

$$\rho = 2.1359 - 5.831 \times 10^{-4} T \tag{12}$$

which is applicable in a temperature range of 1060–1200 K, the unit of density is ρ(g/cm^3) and for T is (K). For viscosity there is

$$\mu = 0.0732 \exp(5601.7 / RT) \tag{13}$$

where the unit of viscosity is μ(cp or 10^{-3} Pa s), T (K) is temperature, and R = 1.98716 (cal/K*mol).

The equation is applicable in a range of 1070–1170 K. The relatively low viscosities of this molten salt make it a favorable component for a eutectic salt mixture. The thermal conductivity is

$$k = -23.43\times10^{-4} + 4.103\times10^{-6}T \quad (14)$$

where k has unit of cal/(cm*s*K = 418.4 W/m-K), temperature T has unit of (K), and the equations is applicable in the range of 1050–1200 K. The ***thermal conductivities*** of molten salt KCl are slightly lower than that of molten NaCl.

$$P_{vap} = 10^{(8.2800-9032/T)} \quad (15)$$

where P_{vap} (mm*Hg = 133.32Pa) is vapor pressure, and T(K) is temperature which is in the range of 1180–1530 K. Obviously the low vapor pressure of molten KCl is helpful for it being used in a eutectic salt mixture.

The specific ***heat capacity*** of molten KCl is around C_p = 73.6 J/mol*K = 987.24 J/kg*K in the temperature range of 1044–2000 K.

3. Properties of Binary Molten Salt

This section surveyed properties of binary molten salts NaCl + $AlCl_3$, KCl + $AlCl_3$. The compositions mentioned in the discussion are all based on mole fractions. The covalent salts $AlCl_3$ and $ZnCl_2$ both have low melting point, while the ionic salts NaCl and KCl both have rather high boiling points or high temperature stability. It is thus promising that the mixture of covalent and ionic eutectic salts has the potential to possess both low melting point and good stability at high temperatures.

3.1. Mixture of NaCl + $AlCl_3$

Eutectic melting point for NaCl + $AlCl_3$ is generally low. For example, the mixture in a mole fraction of 36.8% NaCl + 63.2% $AlCl_3$ has a melting point of T_m = 378–381 K (105–108 ^oC) [66].

The ***densities*** of salt mixture NaCl + $AlCl_3$ in three compositions under molten states at different temperatures are given in Table 2, which are also plotted in Figure 7(a). The more NaCl is included in the mixture, the high the densities are.

Table 2. Density of molten salt NaCl + $AlCl_3$ (% by mole) [66].

T(K)	ρ (kg/m^3)		
	27% NaCl + 73% $AlCl_3$	38.2% NaCl + 61.8% $AlCl_3$	48% NaCl + 52% $AlCl_3$
400			1733
410			1724
420			1716
430			1708
440		1653	1699
450		1644	1691

460	1588	1635	1682
470	1579	1627	1674
480	1570	1618	1666
490	1561	1609	1657
500	1551	1601	1649
510	1542	1592	1641
520	1533	1583	1632
530	1524	1575	1624
540	1515	1566	1615
550	1505		1607
560	1496		1598
570	1487		
580	1478		
590	1469		
600	1459		
610	1450		

27%NaCl + 73%$AlCl_3$: $\rho = 2011 - 0.92 \times T$, Temperature Range : 460–610K (16)

38.2%NaCl + 61.8%$AlCl_3$: $\rho = 2034 - 0.866 \times T$, Temperature Range : 440–540K (17)

48%NaCl + 52%$AlCl_3$: $\rho = 2068 - 0.838 \times T$, Temperature Range : 400–560K (18)

where $\rho(kg/m^3)$ is density and T(K) is temperature.

Viscosities of molten salt mixture NaCl + $AlCl_3$ in seven compositions are obtained from literature [66] as given in Table 3 and illustrated in Figure 7(b). The low viscosities are favorable for the eutectic molten salts being used as heat transfer fluids.

Table 3. Viscosity of liquid NaCl + $AlCl_3$ (% by mole) [66].

T(K)	μ(kg/m*s)						
	50%NaCl 50%$AlCl_3$	45%NaCl 55%$AlCl_3$	40.01%NaCl 59.99%$AlCl_3$	35.04%NaCl 64.96%$AlCl_3$	30.08%NaCl 69.92%$AlCl_3$	25.20%NaCl 74.80%$AlCl_3$	20.28%NaCl 79.72%$AlCl_3$
450			0.0003469	0.0003667			
460	0.0002645	0.000286	0.0003174	0.0003339	0.0003246		
470	0.000245	0.000264	0.0002914	0.0003053	0.000296	0.000259	
480	0.0002277	0.000245	0.0002686	0.0002802	0.0002709	0.000237	0.0001848
490	0.0002123	0.000228	0.0002483	0.000258	0.0002489	0.0002177	0.0001697
500	0.0001984	0.000212	0.0002304	0.0002384	0.0002294	0.0002006	0.0001564
510	0.0001859	0.000199	0.0002143	0.000221	0.0002121	0.0001854	0.0001445
520	0.0001747	0.000186	0.0001999	0.0002054	0.0001967	0.000172	0.000134
530	0.0001645	0.000175	0.000187	0.0001915	0.000183	0.0001599	0.0001246
540	0.0001553	0.000165	0.0001753	0.0001789	0.0001707	0.0001491	0.0001162
550	0.0001469	0.000155	0.0001648	0.0001676	0.0001596	0.0001394	0.0001086
560	0.0001392	0.000147	0.0001552	0.0001574	0.0001496	0.0001306	0.0001017
570	0.0001322	0.000139	0.0001465	0.0001481	0.0001405	0.0001227	0.0000955

50%NaCl + 50%$AlCl_3$: $\mu = 7.2702 \times 10^{-6} \exp(3285.3/RT)$, Range : 460–570 K (19)

45%NaCl + 55%$AlCl_3$: $\mu = 6.8398\times10^{-6}\exp(3413.5/RT)$, Range : 460–570 K (20)

40.01%NaCl + 59.99%$AlCl_3$: $\mu = 5.7828\times10^{-6}\exp(3661.1/RT)$, Range : 450–570 K (21)

35.04%NaCl + 64.96%$AlCl_3$: $\mu = 4.9477\times10^{-6}\exp(3850.2/RT)$, Range : 450–570 K (22)

30.08%NaCl + 69.92%$AlCl_3$: $\mu = 4.2341\times10^{-6}\exp(3966.7/RT)$, Range : 460–570 K (23)

25.20%NaCl + 74.80%$AlCl_3$: $\mu = 3.6622\times10^{-6}\exp(3977.5/RT)$, Range : 470–570 K (24)

20.28%NaCl + 79.72%$AlCl_3$: $\mu = 2.8309\times10^{-6}\exp(3985.8/RT)$, Range : 480–570 K (25)

where μ(kg/m*s) is viscosity, T(K) is temperature, and R = 1.98716 (cal/K*mol).

There is a very limited number of data for the ***thermal conductivity*** of NaCl + $AlCl_3$ [66]. For a mixture in mole fraction of 27%NaCl + 73%$AlCl_3$ (with a melting point of 460 K) the liquid thermal conductivity at 467 K is 0.2217 W/(m K).

Vapor pressures of NaCl + $AlCl_3$ in a dozen of different compositions are shown in Table 4 and Figure 7(c). The corresponding equations of the vapor pressures are also provided in the table.

Table 4. Vapor pressure of NaCl + $AlCl_3$ (% by mole) [66].

	P_{vap} (kPa)											
T(K)	46.21% NaCl 53.79% $AlCl_3$	45.75% NaCl 54.25% $AlCl_3$	44.49% NaCl 55.51% $AlCl_3$	41.94% NaCl 58.06% $AlCl_3$	39.02% NaCl 60.98% $AlCl_3$	37.32% NaCl 62.68% $AlCl_3$	36.94% NaCl 63.06% $AlCl_3$	34.10% NaCl 65.90% $AlCl_3$	33.96% NaCl 66.04% $AlCl_3$	30.72% NaCl 69.28% $AlCl_3$	29.75% NaCl 70.25% $AlCl_3$	26.07% NaCl 73.93% $AlCl_3$
380				0.311								
390				0.453								
400				0.647								
410				0.908	1.871	2.994	3.942					
420		0.381	0.52	1.255	2.629	4.142	5.366					
430		0.511	0.687	1.707	3.636	5.645	7.199	17.715	15.76			
440	0.653	0.676	0.895	2.29	4.954	7.585	9.53	22.465	20.608	45.547		
450	0.803	0.884	1.153	3.033	6.658	10.058	12.46	28.19	26.658	57.151	66.171	
460	0.977	1.143	1.469	3.969	8.835	13.176	16.101	35.026	34.081	71.009	82.26	142.171
470	1.18	1.461	1.852	5.134	11.583	17.064	20.581	43.12	43.119	87.414	101.318	173.96
480	1.413	1.848		6.57	15.015	21.861	26.039	52.626	54.02	106.681	123.714	211.076
490	1.681	2.316		8.325	19.26	27.726	32.631	63.708	67.858	129.14		254.098
500		2.876		10.447	24.458	34.83	40.523	76.536	82.525	155.139		303.627
510		3.541		12.995	30.771	43.367	49.9	91.288	100.738	185.034		360.285
520		4.325		16.028	38.373	53.541	60.955	108.15	122.03	219.201		424.712

46.21%NaCl + 53.79%$AlCl_3$: $P_{vap} = 10^{(4.71496-1771/T)}/760\times101.325$, Range : 440–490K (26)

45.75%NaCl + 54.25%$AlCl_3$: $P_{vap} = 10^{(5.94281-2304.5/T)}/760\times101.325$, Range : 420–520K (27)

44.487%NaCl + 55.513%$AlCl_3$: $P_{vap} = 10^{(5.77583-2177.5/T)}/760\times101.325$, Range : 420–470K (28)

41.938%NaCl + 58.062%$AlCl_3$: $P_{vap} = 10^{(6.72729-2416.6/T)}/760\times101.325$, Range : 380–520K (29)

39.023%NaCl + 60.977%$AlCl_3$: $P_{vap} = 10^{(7.34912-2542.8/T)}/760\times101.325$, Range : 410–520K (30)

37.323%NaCl + 62.677%$AlCl_3$: $P_{vap} = 10^{(7.27205-2427.5/T)}/760\times101.325$, Range : 410–520K (31)

36.954%NaCl + 63.046%$AlCl_3$: $P_{vap} = 10^{(7.09260-2304.9/T)}/760\times101.325$, Range : 410–520K (32)

34.096%NaCl + 65.904%$AlCl_3$: $P_{vap} = 10^{(6.66296-1952.0/T)}/760\times101.325$, Range : 430–520K (33)

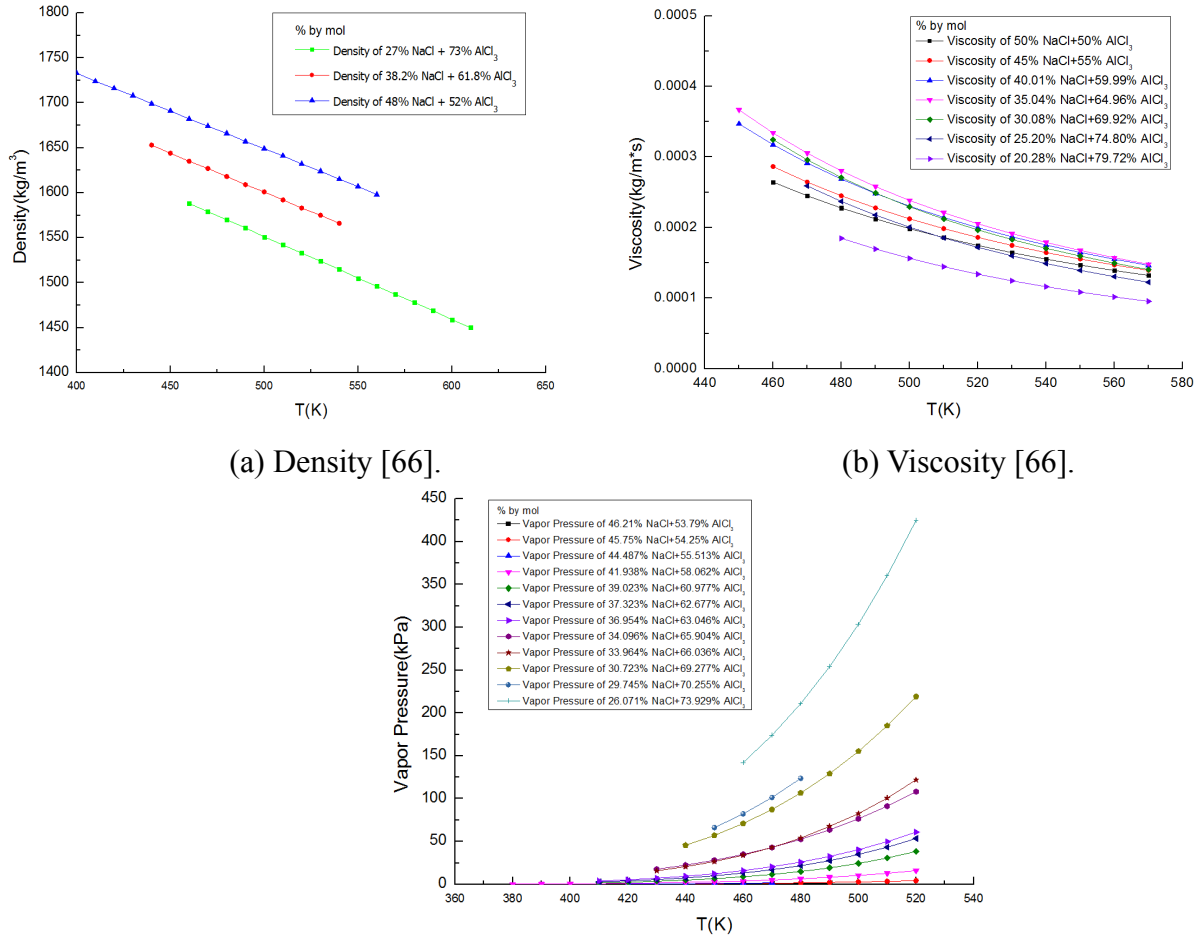
33.964%NaCl + 66.036%$AlCl_3$: $P_{vap} = 10^{(7.20848-2208.4/T)}/760\times101.325$, Range : 430–520K (34)

30.723%NaCl + 69.277%$AlCl_3$: $P_{vap} = 10^{(6.96901-1951.6/T)}/760\times101.325$, Range : 440–520K (35)

29.745%NaCl + 70.255%$AlCl_3$: $P_{vap} = 10^{(7.04376 - 1956.6/T)} / 760 \times 101.325$, Range : 450–480K (36)

26.071%NaCl + 73.929%$AlCl_3$: $P_{vap} = 10^{(7.14703 - 1894.8/T)} / 760 \times 101.325$, Range : 460–520K (37)

where P_{vap} (kPa) is vapor pressure and T(K) is temperature.



(a) Density [66]. (b) Viscosity [66].

(c) Vapor Pressure [66].

Figure 7. Properties of molten salt mixture NaCl+$AlCl_3$.

3.2. Mixture of KCl + $AlCl_3$

The melting point of this binary salt system is relatively low. For the mole composition of 33%KCl + 67%$AlCl_3$ there is T_m = 401 K (128 ^oC) [66]. The densities for mixtures in four different compositions at different temperatures are shown in Table 5 and drawn in Figure 8 (a) [66]. Vapor pressures of the mixtures at four different compositions are shown in Table 6 and Figure 8(b) [66].

Table 5. Density of liquid KCl + $AlCl_3$ (% by mole) [66].

T(K)	ρ (kg/m^3)			
	20%KCl 80%$AlCl_3$	33.33%KCl 66.67%$AlCl_3$	50.03%KCl 49.97%$AlCl_3$	52.78%KCl 47.22%$AlCl_3$
480	1543			
500	1523	1594		

520	1503	1578			
540	1483	1562			
560		1547			
580		1531			
600		1515			
620		1499			
640		1483			
660		1468			
680		1452			
700		1436			
720		1420			
740		1404	1466		
760		1389	1452		
780		1373	1439		
800			1426		
820			1413		
840			1399		
860			1386		
880			1373		
900			1360		
920			1346		
940			1333		
960			1320	1388	
980			1307	1376	
1000			1293	1363	
1020			1280	1351	
1040			1267	1339	

20%KCl + 80%$AlCl_3$: $\rho = 2025.2 - 1.0038 \times T$, Range : 480–540K (38)

33.33%KCl + 66.67%$AlCl_3$: $\rho = 1988.9 - 0.7901 \times T$, Range : 500–780K (39)

50.03%KCl + 49.97%$AlCl_3$: $\rho = 1955.6 - 0.6622 \times T$, Range : 740–1040K (40)

66.66%KCl + 33.34%$AlCl_3$: $\rho = 1973.4 - 0.6101 \times T$, Range : 960–1040K (41)

where ρ(kg/m^3) is density and T(K) is temperature.

Table 6. Vapor pressure of liquid KCl + $AlCl_3$ [66].

T(K)	P_{vap} (kPa)			
	49.9%KCl + 50.01%$AlCl_3$	51.5%KCl + 48.5%$AlCl_3$	57.6%KCl + 42.4%$AlCl_3$	63.8%KCl + 36.2%$AlCl_3$
870	0.613			
880	0.72			
890	0.867			
900	1.027			
910	1.2	0.547		
920	1.413	0.68	0.587	
930	1.653	0.84	0.72	
940	1.933	1.04	0.88	
950	2.24	1.267	1.08	0.907
960	2.6	1.547	1.307	1.08
970	3.013	1.88	1.573	1.293

980	3.466	2.28	1.893	1.547
990	3.986	2.746	2.28	1.827
1000	4.573	3.293	2.72	2.173
1010	5.226	3.933	3.226	2.56
1020	5.96	4.693	3.84	3
1030	6.773	5.573	4.533	3.52
1040	7.679	6.599		
1050	8.693	7.786		
1060	9.813	9.159		
1070	11.052	10.732		

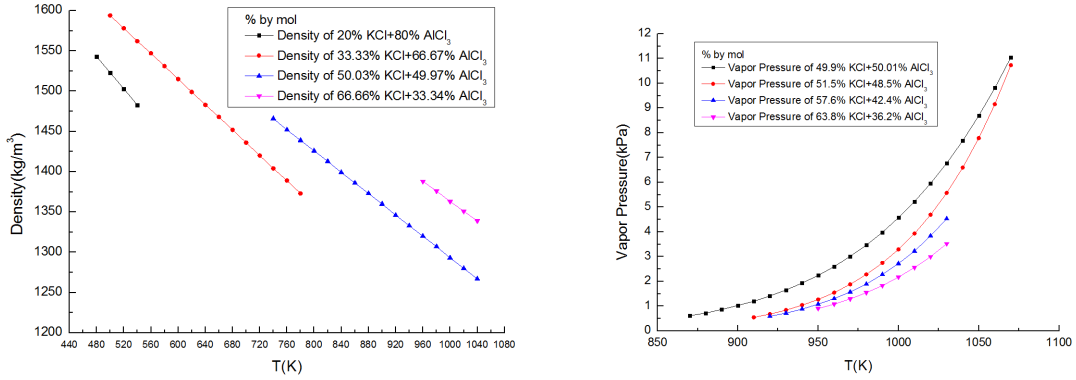
49.9%KCl + 50.01%$AlCl_3$: $P_{vap} = (10^{7.395-5860/T})/760\times101.325$, Range: 870–1070K (42)

51.5%KCl + 48.5%$AlCl_3$: $P_{vap} = (10^{9.2386-7846/T})/760\times101.325$, Range: 910–1070K (43)

57.6%KCl + 42.4%$AlCl_3$: $P_{vap} = (10^{8.943-7634/T})/760\times101.325$, Range: 920–1030K (44)

63.8%KCl + 36.2%$AlCl_3$: $P_{vap} = (10^{8.4231-7212/T})/760\times101.325$, Range: 950–1030K (45)

where P_{vap} is in kPa, unit of temperature is in K.



(a) Density [66]. (b) Vapor pressure [66]

Figure 8. Properties of molten salt mixture KCl+$AlCl_3$.

4. Properties of Ternary Molten Salt Systems

This section surveyed properties of two ternary molten salts, NaCl + KCl + $AlCl_3$ and NaCl + KCl + $ZnCl_2$. All the compositions referred to are based on mole fraction.

4.1. NaCl+KCl+$AlCl_3$

There are two eutectic points for NaCl + KCl + $AlCl_3$ [66]. The one with a composition of 20%NaCl + 16.5%KCl + 63.5%$AlCl_3$ has a melting point of T_m = 361.9 K (88.9 °C). The densities of the ternary salt with different compositions at different temperatures are given in Table 7 and Figure 9. There is no vapor pressure data found for this ternary system. However, the high vapor pressure of $AlCl_3$ could make this system to have high vapor pressures and thus not suitable as a HTF.

Table 7. Density of liquid NaCl + KCl + $AlCl_3$ (% by mole) [66].

T(K)	ρ (kg/m^3)						
	50%NaCl +40%KCl +10%$AlCl_3$	55%NaCl +25%KCl +20%$AlCl_3$	60%NaCl +30%KCl +10%$AlCl_3$	60%NaCl +20%KCl +20%$AlCl_3$	60%NaCl +10%KCl +30%$AlCl_3$	65%NaCl +25%KCl +10%$AlCl_3$	65%NaCl +10%KCl +25%$AlCl_3$
430			1716.7	1699.9		1681.9	1676.4
440		1707.7	1707.9	1690.2		1673.1	1666.2
450		1698.7	1699.1	1680.5		1664.4	1656.0
460		1689.6	1690.3	1670.8		1655.6	1645.8
470		1680.6	1681.5	1661.1	1672.7	1646.8	1635.6
480		1671.6	1672.6	1651.4	1664.4	1638.0	1625.4
490					1656.2		
500	1674.5				1648.0		
510	1665.3				1639.8		
520	1656.0				1631.6		
530	1646.8						
540	1637.6						

50%NaCl+40%KCl+10%$AlCl_3$: $\rho = 2136 - 0.923 \times T$, for T(K) in 500–540K (46)

55%NaCl+25%KCl+20%$AlCl_3$: $\rho = 2105 - 0.903 \times T$, for T(K) in 440–480K (47)

60%NaCl+30%KCl+10%$AlCl_3$: $\rho = 2096 - 0.882 \times T$, for T(K) in 430–480K (48)

60%NaCl+20%KCl+20%$AlCl_3$: $\rho = 2117 - 0.97 \times T$, for T(K) in 430–480K (49)

60%NaCl+10%KCl+30%$AlCl_3$: $\rho = 2059 - 0.822 \times T$, for T(K) in 470–520K (50)

65%NaCl+25%KCl+10%$AlCl_3$: $\rho = 2059 - 0.877 \times T$, for T(K) in 430–480K (51)

65%NaCl+10%KCl+25%$AlCl_3$: $\rho = 2115 - 1.02 \times T$, for T(K) in 960–1170K (52)

where unit of density is ρ (kg/m^3) and T is in (K).

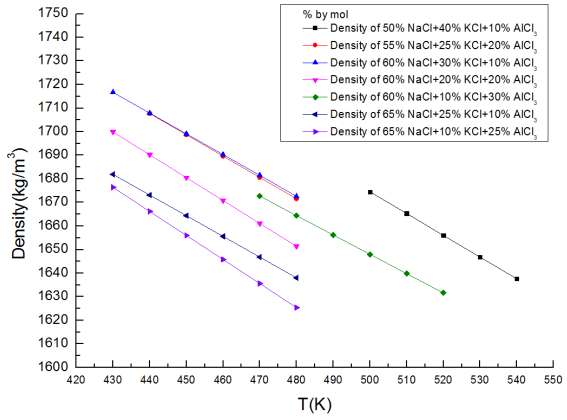


Figure 9. Densities of ternary mixture NaCl + KCl + $AlCl_3$ [66] **at various compositions.**

4.2. NaCl + KCl + $ZnCl_2$

There are three eutectic mixtures for this ternary system that may have melting temperatures below 250 °C. One particular composition is 20% NaCl + 20% KCl + 60% $ZnCl_2$ that has a melting point of T_m = 476 K (203 °C). Because of the relatively low vapor pressure of $ZnCl_2$, this eutectic

salt may also have a low vapor pressure and thus is very promising to be a HTF. The densities of this eutectic mixture are given in Table 8 and Figure 10 (a). Viscosities of the salt are given in Table 9 and Figure 10(b).

Table 8. Densities of the molten salt 20%NaCl + 20%KCl + 60%$ZnCl_2$ (% by mole) [74]**.**

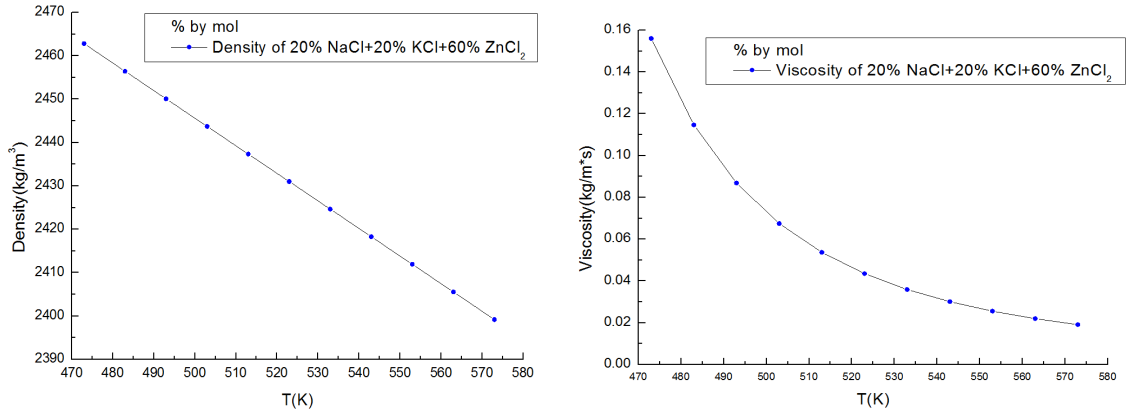
T(K)	ρ(g/cm^3)	ρ(kg/m^3)
473	2.46	2462.8
483	2.46	2456.44
493	2.45	2450.08
503	2.44	2443.72
513	2.44	2437.36
523	2.43	2431
533	2.42	2424.64
543	2.42	2418.28
553	2.41	2411.92
563	2.41	2405.56
573	2.4	2399.2

$\rho = 2.59 - 6.36 \times 10^{-4}(T - 273)$; where the units are ρ(kg/m^3), and T(K), in the range of 473–573K. (53)

Table 9. Viscosity of the molten salt 20%NaCl + 20%KCl + 60%$ZnCl_2$ (% by mole) [74]

T(K)	**μ(cp)**	**μ(kg/m*s)**
473	155.9932	0.15599
483	114.6464	0.11465
493	86.8344	0.08683
503	67.5008	0.0675
513	53.6699	0.05367
523	43.5235	0.04352
533	35.9132	0.03591
543	30.0916	0.03009
553	25.5594	0.02556
563	21.9752	0.02198
573	19.1002	0.0191

$\mu = 1.23 \times 10^{-2}\sqrt{T}\exp\left(\frac{1.21 \times 10^3}{T - 283}\right)$; where the units are μ(cp), and T(K), within the range of 473–573K. (54)



(a) Density [74] (b) Viscosity [74]

Figure 10. Properties of salt (20%NaCl + 20%KCl + 60%$ZnCl_2$ (% by mole)).

5. Conclusion and Outlook

This paper gave a brief introduction to the currently available high temperature HTFs and the necessity of developing new-generation materials for even higher working temperatures (at least 800 ^oC) for the goal of high thermal efficiency in concentrated solar thermal power plant.

The authors particularly gave attention to possible mixtures of ionic and covalent halide salts for the potential of creating a eutectic salts to meet the basic criteria for a HTF. Low cost and almost unlimited reserve of halide salts is also important due to the large demand in industry. The reviewing has found that some binary and ternary halide salts could have eutectic mixtures with low melting points, which therefore are recommendable for the components of a HTF.

For those halide salts recommended as the components of mixture eutectic molten salts, available properties of the individual candidate and binary and ternary mixtures are surveyed and presented for reference of further studying and investigation of all the properties that remaining unknown so far. Table 10 summaries the availability of results obtained from literature. Some key conclusions from the survey are drawn:

(1) It is understood that the three covalent halide salts $AlCl_3$, $ZnCl_2$, and $FeCl_3$ have relatively low melting points which may contribute to the low eutectic melting point for a mixture of ionic and covalent halide salts. However, the relatively very high vapor pressures of $AlCl_3$ and $FeCl_3$ are of concerns to the possible high vapor pressures of eutectic salt mixtures.

(2) Two binary eutectics salts NaCl-$AlCl_3$ and KCl-$AlCl_3$ show low eutectic melting points below 250 ^oC. The system of NaCl-$AlCl_3$ still has rather high vapor pressure which may come from the high vapor pressure of $AlCl_3$. However, the eutectic of KCl-$AlCl_3$ show relatively lower vapor pressure compared to that of NaCl-$AlCl_3$. This is an indication that KCl is an important component to suppress the vapor pressure of eutectic mixtures. The viscosities of these two binary systems are low and very favorable.

(3) Two ternary eutectic salts from the system of NaCl-KCl-$AlCl_3$ and NaCl-KCl-$ZnCl_2$ showed low viscosities that are very favorable for heat transfer fluids. The densities of the two eutectic salts are also acceptable. However, there are no other thermal and transport properties, which need research and investigation.

Last but not least, the chemical corrosion of the surveyed salts to metals of pipes and containers is a very important issue. A detailed survey is yet to be carried out. However, one recent article [75]

showed results of corrosion of Hastelloys in 13.4NaCl–33.7KCl–52.9$ZnCl_2$ (mol%) eutectic system. Evaluated from both electrochemical method and immersion test, the type N Hastelloy showed a higher corrosion rate of > 150 μm per year at 500 ^oC, but the Hastelloy C-276 exhibited the lowest corrosion rate of 40 μm per year at 500 ^oC. More results on corrosions of these salts to metals are expected to see in the future.

Referring to the available properties for these halide salts, the researchers teamed-up from the University of Arizona, Georgia Institute of Technology, and Arizona State University have been investigating details of properties of ternary salt systems (KCl-NaCl-AlCl3), (KCl-NaCl-$ZnCl_2$), and (KCl-NaCl-$FeCl_3$), as well as quaternary systems. Simulations and fast screening method are applied for searching eutectic salt compositions; while experimental tests are followed up to measure all the properties, including corrosion to metals, for evaluation of the suitability for a HTF.

Table 10. Summary of the availability of physical properties of $AlCl_3$, $ZnCl_2$, $FeCl_3$, NaCl, KCl, and their mixtures.

	Single Molten Salt					Binary Molten Salt			Ternary Molten Salt	
	$AlCl_3$	$ZnCl_2$	$FeCl_3$	NaCl	KCl	NaCl+$AlCl_3$	KCl+$AlCl_3$	NaCl+KCl	NaCl+KCl +$AlCl_3$	NaCl+KCl +$ZnCl_2$
Density	✓	✓	×	✓	✓	✓	✓	✓	✓	✓
Viscosity	✓	✓	×	✓	✓	✓	×	✓	×	✓
Thermal Conductivity	×	×	×	✓	✓	×	×	×	×	×
Specific Heat Capacity	✓	✓	✓	✓	✓	×	×	×	×	×
Vapor Pressure	✓	✓	✓	✓	✓	✓	✓	✓	×	×
Melting Point	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

✓ : Data obtained from literature; × : No data available from literature

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

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