

NOVEL IONIC LIQUID THERMAL STORAGE FOR SOLAR THERMAL ELECTRIC POWER SYSTEMS

Banqiu Wu
Center for Green Manufacturing
PO Box 870202, The University of Alabama
Tuscaloosa, AL 35487-0202
Phone: (205)348-4423
banqiu@bama.ua.edu

Ramana G. Reddy
Department of Metallurgical and Materials Engineering
PO Box 870202, The University of Alabama
Tuscaloosa, AL 35487-0202
Phone: (205)348-4246
rreddy@coe.eng.ua.edu

Robin D. Rogers
Center for Green Manufacturing
PO Box 870202, The University of Alabama
Tuscaloosa, AL 35487-0202
Phone: (205)348-4323
rdrogers@bama.ua.edu

ABSTRACT

Feasibility of ionic liquids as liquid thermal storage media and heat transfer fluids in a solar thermal power plant was investigated. Many ionic liquids such as [C₄min][PF₆], [C₈mim][PF₆], [C₄min][bistrifluoromethane sulfonylimide], [C₄min][BF₄], [C₈mim][BF₄], and [C₄min][bistrifluoromethane sulfonylimide] were synthesized and characterized using thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), nuclear magnetic resonance (NMR), viscometry, and some other methods. Properties such as decomposition temperature, melting point, viscosity, density, heat capacity, and thermal expansion coefficient were measured. The calculated storage density for [C₈mim][PF₆] is 378 MJ/m³ when the inlet and outlet field temperatures are 210°C and 390°C. For a single ionic liquid, [C₄mim][BF₄], the liquid temperature range is from -75°C to 459°C. It is found that ionic liquids have advantages of high density, wide liquid temperature range, low viscosity, high chemical stability, non-volatility, high heat capacity, and high storage density. Based on our experimental results, it is concluded that ionic liquids could be excellent liquid thermal storage media and heat transfer fluids in solar thermal power plant.

NOMENCLATURE

C _p	Heat capacity, J/(kg K)
E	Storage density, MJ/m ³
Pr	Prandtl number
T _{in}	Inlet temperature, °C
T _{out}	Outlet temperature, °C
T _{dec}	Decomposition temperature, °C
T _{mp}	Melting point temperature, °C
k	Thermal conductivity, W/(m K)
μ	Viscosity, Pa S
ρ	Density, kg/m ³

INTRODUCTION

Solar energy is the most abundant energy source on the earth. Compared with other energy from oil, coal and nuclear reaction, solar energy is clean and in unlimited supply. Solar energy usually is collected and transferred to thermal energy to heat room and water, or generate electricity. Energy transformation of solar energy - thermal energy - electricity is the most important application of solar energy.

Because the solar energy availability depends on time, weather condition, and latitude, and the electricity demand varies with time, the energy originally from solar energy needs to be stored. This energy can be stored as thermal energy or electricity, but storage in thermal energy is considered the more economic method.

Currently thermal oil and molten salt are used as liquid storage media. The main problems for oil media are the low decomposition temperature (e.g. 300°C) and for molten salt media it is its high melting point (e.g. 220°C). The low decomposing temperature limits the energy storage and high melting point can cause molten salt freezing in evening or cold weather, resulting in high operating costs.

The rate of solar energy intercepted by the earth is about 5,000 times greater than the sum of all other energy sources, but less than 0.5 percent is represented in the kinetic energy of the wind, waves and in photosynthetic storage in plants. The amount of the solar energy intercepted by earth is only one thousandth of one million of the total released energy in the sun.

A wide variety of equipment is readily available to capture solar energy and use it for space and water heating, and for electricity generating. The three major components for solar thermal energy utilization systems are the solar energy collector, the energy storage system, and the steam

generator used for the turbine-electric generator. Thermal energy is usually collected by parabolic trough, transferred to thermal storage by a heat transfer fluid, and then transferred to steam generator by storage media. For an active thermal energy storage in a direct system, heat transfer fluid collects the solar heat and serves also as storage medium. The solar energy system costs are strongly dependent on the properties of thermal storage media and heat transfer fluid.

For most industrial applications, water is the most popular heat transfer fluid. It has high latent thermal energy, high thermal conductivity, high specific heat, and high density with moderate viscosity. The biggest difficulties for water as a heat transfer fluid is the limited range of temperature over which it can be used. Theoretical liquid range is between 0°C and 100°C, but the practical temperature range for water used as heat transfer fluid is much less than 100°C, because of the high vapor pressure at near boiling point. The extension of the application temperature range to below freeze point can be accomplished by using antifreeze (e.g., ethylene glycol-water mixture), but the extension over the boiling point of the aqueous system is extremely difficult.

High pressure is needed to keep water in the liquid state when the temperature is over 100°C, which could cause very high costs for the related pressure vessels and pipes. High temperature water (over 100°C) was suggested for many industrial applications (Lieberg, 1958), but it is not suitable as a heat transfer fluid nor as thermal media for a solar energy power plant.

Gases are sometimes used as heat transfer fluids instead of water when a wider temperature range is required, although they have low density, low specific heat capacity, and low thermal conductivity. These properties make gaseous heat transfer fluids not as effective as liquid. A gaseous heat transfer fluid usually is only used when liquid cannot be used, such as at high temperature.

Thermal oils can keep their liquid phase up to about 300°C and can be used as thermal storage media and heat transfer fluids, but their applications are limited by some intrinsic disadvantages such as low decomposition temperature, low density, inflammability, high vapor pressure, harmfulness, and low chemical stability.

Liquid metals and molten salts were proposed as heat transfer fluids for high temperatures such as 250 to 1000°C (Fraas and Ozisik, 1965; and MacPherson et al, 1960). A practical molten salt medium is a mixture of sodium nitrite, sodium nitrate, and potassium nitrate. Due to the avoidance of high pressure, the wall thickness of the piping and the pump casings, heat exchangers, and other items of equipment were much lower than those required for high-pressure steam systems operating in this temperature range. One problem is that the heat exchanger system has to be preheated to ensure that liquid metal and molten salts

remain liquid. When the temperature is not high enough, the liquids or molten salts freeze and cause operation problems. A liquid metal heat transfer medium was commercialized in 1923 (Emmet, 1924) and a molten salt heat transfer medium was commercialized in 1937 (Kirst et al, 1940). Although there are some operation problems as described above, the molten salts have been used in cracking units in the petroleum refining industry. The reason is that there is no better heat transfer medium available.

Ionic liquids are a group of salts with a wide temperature range for the liquid phase. The main advantages include the wide liquid temperature range, high heat capacity, high density, high thermal and chemical stability, low vapor pressure, and non-harmfulness. We are not aware of examples where ionic liquids are used as liquid storage media and heat transfer fluids.

In this study, ionic liquids were synthesized and their relevant properties were investigated for application as liquid thermal storage media and heat transfer fluids.

EXPERIMENTS AND RESULTS

1. Synthesis Procedures of Ionic Liquids

The experimental setup is shown in Fig. 1. The synthesis procedures for different ionic liquids are described in the following.

The starting material of chlorides such as 1-butyl-3-methylimidazolium chloride (C_4mimCl) was synthesized in our laboratory. 1-methylimidazole and 1-chlorobutane was put in a glass container under argon atmosphere for 4 days at 70°C with magnetic agitation. After the reaction was completed, the product and unreacted starting materials separated in two liquid phases. The top layer consists of impurities and was discarded. The product was washed with ethylacetate for several times. Vacuum was used for the complete removal of unreacted materials and washing liquid.

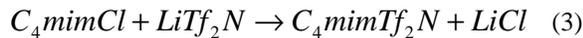
For the ionic liquids with the $[PF_6]$ anion, 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6) is taken as an example of the synthesis of these ionic liquids. The starting materials are C_4mimCl and HPF_6 . Liquid HPF_6 was added to C_4mimCl slowly at ambient temperature with magnetic agitation. After the reaction, the product and unreacted starting materials separated in two liquid layers. The top layer contains the starting materials and the bottom is the product. First, the top layer was removed, and then some water was put in the container. It was agitated at room temperature for a few minutes and the top layer – the aqueous phase containing impurities was poured. The above washing operation was repeated for several times. Vacuum was used on the container to completely remove the unreacted materials and washing materials. The reaction is shown in Eq. (1).



For the ionic liquids with the $[BF_4]$ anion such as 1-butyl-3-methylimidazolium tetrafluoroborate (C_4mimBF_4), the starting materials are C_4mimCl and HBF_4 . The synthesis procedure is similar to that of ionic liquids with the $[PF_6]$ anions. The reaction is shown in Eq. (2). The products form one liquid phase, and the HCl is removed by the liquid-liquid extraction using methylene chloride. The product is also dried using vacuum.



For the ionic liquids with the $[Tf_2N]$ anion, e.g. 1-butyl-3-methylimidazolium bistrifluoromethane sulfonylimide (C_4mimTf_2N), the starting materials are C_4mimCl and $LiTf_2N$, i.e. $[Li(CF_3SO_2)_2N]$. The synthesis procedure is similar with the ionic liquids with the anions of $[PF_6]$. The reaction is shown in Eq. (3).



2. Experimental Results

Ionic liquids were characterized using NMR, TGA, DSC, and DTA. The DSC result of C_4mimPF_6 ionic liquid is shown in Fig. 2, which indicates the melting point at about 4°C. The decomposition temperature is shown by TGA (e.g. C_8mimPF_6 ionic liquid) in Fig. 3. NMR results (C_4mimPF_6) are shown in Fig. 4 (Proton), Fig. 5 (Carbon-13), and Fig. 6 (Fluorine-19). They indicate that there are very little peaks for starting materials and the reaction was almost completed.

The properties of ionic liquids are listed in Table 1.

DISCUSSION

1. Current Heat Transfer Fluid and Thermal Storage Media

Current molten salt heat transfer fluids and thermal media are a mixture of 60% $NaNO_3$ and 40% KNO_3 (Pilkington, 2000). The temperature range for the liquid is 220-600°C. The main disadvantage of this salt mixture is the high melting point. In the evening, especially in the winter, the salt can freeze and block the pipeline system, which makes operation and maintenance very difficult. In order to overcome these problems, some auxiliary facilities need to be installed, which could increase the investment and operation costs.

Santotherm 55 is a common thermal oil used as thermal storage media and heat transfer fluid. It allows working temperatures above 300°C without decomposing (Camacho et al, 1997). The main properties are listed in Table 2. One of the main characteristics of this oil is its low thermal conductivity. Furthermore, its density is highly dependent on its temperature, which permits the use of just one storage tank to contain both the hot and the cold oil in thermal stratification (the thermocline effect). An inlet field temperature of 210°C and an outlet field on of 290°C is obtained. The main disadvantages of the thermal oils are low density, low thermal capacity, and low decomposing temperature, resulting in a low energy storage.

2. Properties of Ionic Liquids

Ionic liquids are salts, usually having low melting points. The important properties include high heat capacity, high density, high thermal conductivity, extremely low volatility, non-flammability, high thermal stability, wide temperature range for liquid, many variations in compositions, and large number of possible variations in cation and anion conformation allowing fine-tuning of the ionic liquid properties for specific applications.

Typical ionic liquid cations are N-butylpyridinium and 1-alkyl-3-methylimidazolium (alkyl mim) or 1,3-kialkylimidazolium (RR'im). Their molecular structures are shown in Fig. 7. Common anions are $[PF_6^-]$ and $[BF_4^-]$. Other anions include triflate $[TfO^-]$ - $CF_3SO_2^-$, nonaflate $[NfO^-]$ - $CF_3(CF_2)_3SO_2^-$, bistrifluoromethane sulfonylimide $[Tf_2N^-]$ - $(CF_3SO_2)_2N^-$, trifluoroacetate $[TA^-]$ - $CF_3CO_2^-$ and heptafluorobutanoate $[HB^-]$ - $CF_3(CF_2)_3CO_2^-$.

In this study, ionic liquids synthesized include $C_{10}mimPF_6$, C_8mimPF_6 , C_4mimPF_6 , $C_{10}mimBF_4$, C_8mimBF_4 , C_4mimBF_4 , C_4mimTf_2N , and $C_4mim-AlCl_4$.

Some properties of the synthesized ionic liquids were measured. Thermogravimetric analysis (TGA) is a useful tool for the investigation of material properties (Reddy and Inturi, 1999) and was used for measurement of the decomposition temperature. Differential scanning calorimeter (DSC) was used for the measurement of points. Viscosities of ionic liquids were measured using a viscometer. The ionic liquids were also characterized using liquid chromatography and gas chromatography (GC) to ensure the ionic liquid composition and quality. Other properties such as air and water stability, water content and



Fig. 1. Experimental setup.

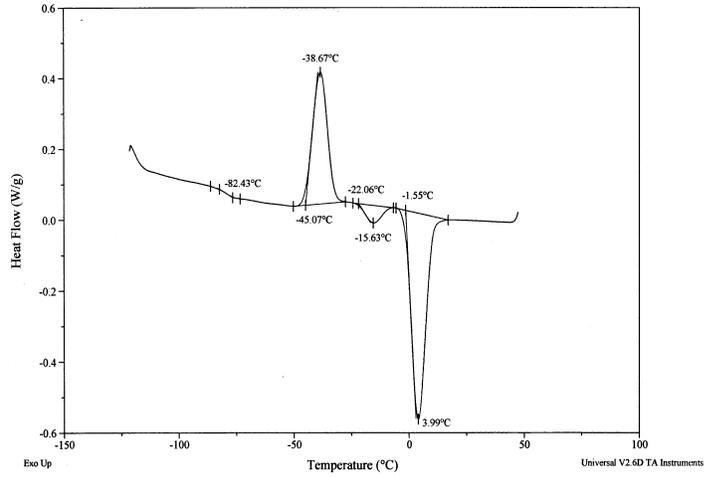


Fig. 2. DSC result of C_4mimPF_6 ionic liquid

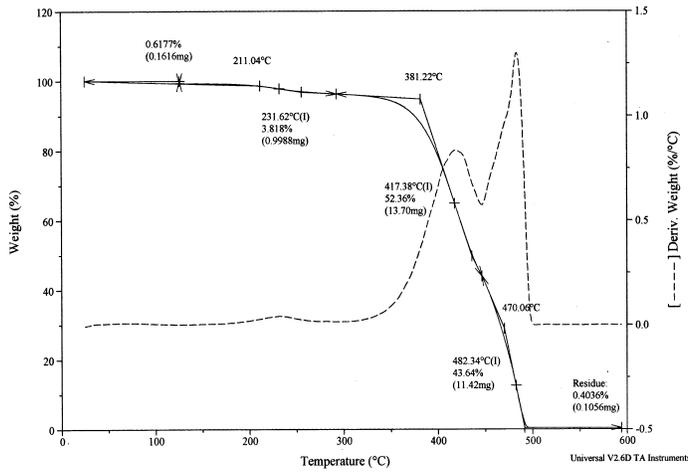


Fig. 3. TGA result of C_3mimPF_6 ionic liquid

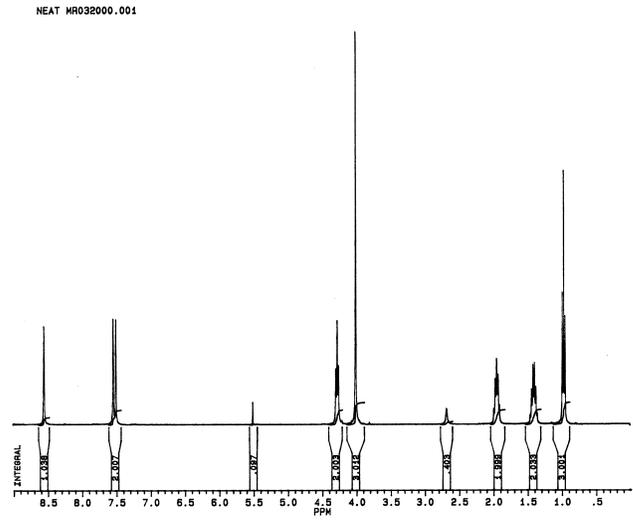


Fig. 4. NMR result of C_4mimPF_6 ionic liquid (Proton)

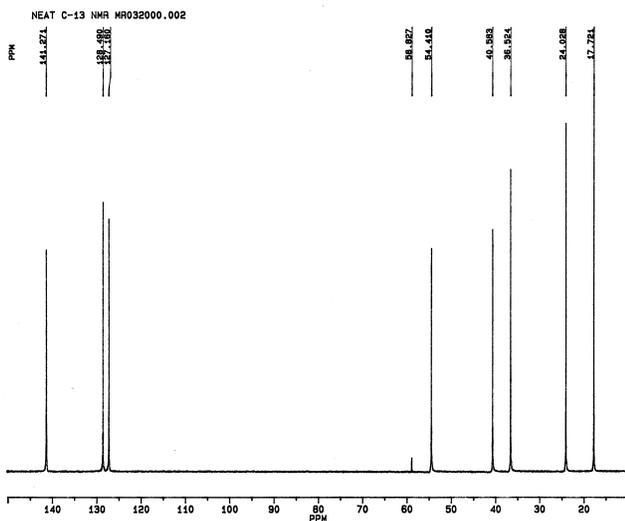


Fig. 5. NMR result of C_4mimPF_6 ionic liquid (Carbon-13)

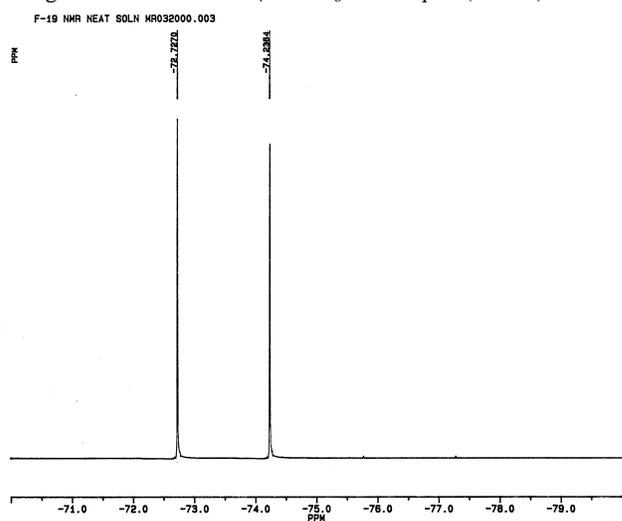


Fig. 6. NMR result of C_4mimPF_6 ionic liquid (Fluorine-19)

TABLE 1. SOME PROPERTIES OF IONIC LIQUIDS.

Ionic liquid	Melting point, °C	Decomposition point, °C	Viscosity at 25°C, mPa s	Density at 25°C, kg/m ³
[C ₁₀ mim][PF ₆]	34	390	--	
[C ₈ mim][PF ₆]	-75	416	--	
[C ₄ mim][PF ₆]	4	390	312	
[C ₁₀ mim][BF ₄]	-77.5	--	--	
[C ₈ mim][BF ₄]	--	--	--	
[C ₄ mim][BF ₄]	-75	407	219	1119
[C ₄ mim][bistriflylimide]	-89	402	54.5	

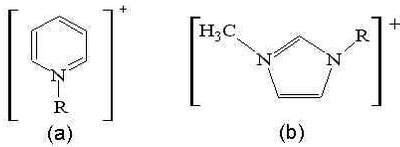


Fig. 7. Typical cations
(a) N-butylpyridinium, (b) alkyl mim or RR'im

immiscibility, and electrochemical properties were also investigated.

By different combination of anions and cations, different ionic liquids can be obtained such as (CF₃SO₂)₂NRmim, RmimClO₄, RmimBF₄, RmimPF₆, and (CF₃SO₂)₃CRmim. Each ionic liquid possesses different physical properties. One example of physical property change with anions is illustrated by melting point on Table 3.

Investigations on the properties of ionic liquids were reported in our previous studies (Hunddleston, 1998; Rogers, 1999). The decomposition temperatures of several ionic liquids synthesized in the current study now exceed 410°C, which is much higher than 300°C as found for other ionic liquids (Freemantle, 1998).

3. Storage Capacity of Ionic Liquids

In our current study, many ionic liquids were synthesized and characterized. Take C₈mimPF₆ as an example for the calculation of storage capacity. The liquid range was -75 to 416°C, heat capacity 2500 J/kg K, and density 1400 kg/m³. These properties allow them to be used as thermal storage media and heat transfer fluids for solar power plants.

The storage density (E) can be calculated by Eq. (4) when inlet and outlet field temperatures are 210°C and 390°C, respectively.

This value is much higher than that of the thermal oil (59 MJ/m³) (Camacho et al, 1997).

The properties of ionic liquids are strongly dependent on the anion, the cation, and the composition. An important advantage of ionic liquids is that the anion, the cation, and

the composition can be arranged based on the demanded properties. By the different combinations of anion and cation, basic composition of ionic liquid for thermal storage media and heat transfer fluid can be obtained. Through mixing of different ionic liquids, like the mixing of different molten salts, the composition of ionic liquids can be further optimized.

$$\begin{aligned}
 E &= \rho C_p (T_{out} - T_{in}) \\
 &= 1400 \frac{\text{kg}}{\text{m}^3} \times 2500 \frac{\text{J}}{\text{kg K}} \times (390 - 120) \text{K} \\
 &= 378 \times 10^6 \frac{\text{J}}{\text{m}^3} = 378 \frac{\text{MJ}}{\text{m}^3}
 \end{aligned}
 \tag{4}$$

TABLE 2. MAIN PROPERTIES OF THERMAL OIL AND C₈MIMPF₆ IONIC LIQUID.

Properties at 25°C	Thermal oil	Ionic liquid
Density ρ _f , kg/m ³	886.2	1400
Specific thermal capacity C _p , J/kg K	1907	2500
Maximum applicable temperature, °C	300	416
Storage density, MJ/m ³	59	378
Thermal conductivity k, W/m K	0.1891	--
Dynamic viscosity μ, Pa S	0.0105	--
Prandlt number Pr	160.5	--

TABLE 3. EFFECT OF THE ANIONS ON MELTING POINTS OF IONIC LIQUIDS

Ionic liquid	Melting point, °C
[emim][NO ₃]	38
[emim][NO ₂]	55
[emim][MeCO ₂]	-45
[emim] ₂ [SO ₄]	70
[emim][PF ₆]	58-60
[emim][TfO]	-9
[emim][NfO]	28
[emim][Tf ₂ O]	-4
[emim][TA]	-14

Although ionic liquids are not new, only in the last few years has much attention been paid to them and since then many new ionic liquids have been synthesized (Koch et al, 1998; and Sherif et al, 1998). Ionic liquids have excellent properties as heat transfer fluids and thermal storage media. Our data show that there is a possibility that current thermal transfer fluid and storage media such as the molten salts and thermal oils can be replaced with ionic liquids.

TABLE 4. COMMON METAL AND MOLTEN SALT HEAT TRANSFER MEDIA AND THEIR PROPERTIES

Heat transfer media	Melting point, °C	Boiling point, °C	Note
Na	97.8	892	Inflammable
K	63.7	760	Inflammable
NaK	--	--	Inflammable
Li	180.5	1330	Inflammable
Pb	327.4	1725	T _{mp} too high
Bi	271.3	1560	T _{mp} too high
Hg	-38.4	357	Very toxic
NaNO ₃	306.8	380 d	Explosive
NaNO ₂	271	320 d	Toxic
KNO ₃	129	400 d	Explosive

d - decomposition at this temperature

4. Optimization of Ionic Liquids by Combination of Anions and Cations

The properties of ionic liquids depend on the ionic structure of anion and cation. Cations are typically big, bulky, and asymmetrical, accounting for the low melting points. The anions contribute more to the overall characteristics of the ionic liquids and determine the air and water stability. One of the most important properties of ionic liquids is that melting point can be easily changed by structural variation of one of the ions or combining different ions.

By the combination of anions and cations, it is found that the ionic liquids such as C₈mimPF₆, C₄mimBF₄, and C₄mimTf₂N have excellent thermal stability for the applications as thermal transfer fluids and liquid storage media, as shown in Table 1.

5. Composition Optimization by Mixing of Different Ionic Liquids

Ionic liquids are salts, but the temperature ranges for these liquids are wider than the molten salts currently used for thermal storage media. Table 4 lists the temperature range of molten salts currently used as thermal storage media and heat transfer fluids before and after mixing. Table 5 shows the temperature range of individual molten salts and the mixings of different molten salts. After mixing of different salts, the liquid temperature range can

be significantly increased.

In this study, different ionic liquids were mixed for the optimization of the composition. An ionic liquid comprising 50% of [C₄mim BF₄] (T_{dec}=407°C) and 50% of [C₆mim Tf₂N] (T_{dec}=341°C) has a higher decomposition temperature than the individual ionic liquids (T_{dec}=427°C after mixing). The optimization via mixing of different ionic liquids is in progress.

TABLE 5. MOLTEN SALT LIQUID RANGE BEFORE AND AFTER MIXING (PILKINGTON, 2000)

Individual molten salt	Composition 1	Composition 2
NaNO ₃ (307-380°C)	7%	60%
NaNO ₂ (271-320°C)	40%	--
KNO ₃ (129-400°C)	53%	40%
Liquid rang after mixing	142°C -	220 - 600°C

6. Feasibility as Thermal Storage Media and Heat Transfer Fluids

The experimental results indicate that the properties of ionic liquids meet main technical requirements for liquid storage media and heat transfer fluids. These requirements include high decomposition temperature, wide temperature range for liquids, high density, high heat capacity, low viscosity, and low vapor pressure.

7. Economic Analysis

Ionic liquids, which will be used as the thermal storage media and heat transfer fluids, are those that were developed recently. Their industrial applications are under development and price for large quantities currently is not available. Price of starting materials for the ionic liquid synthesis in a very small quantity is about \$ 1.3 - 6 /lb. The price in large quantity is difficult to estimate at the present time. The starting material price of ionic liquids is strongly dependent on the quantity of the materials. When the industrial price of the starting materials becomes available, a reasonable estimation of the costs of ionic liquids can be made. In the price estimation for the practical applications, items such as energy consumption, labor fees, and taxes should also be considered.

Based on the currently available data, several ionic liquids technically meet the requirement as the thermal storage media and heat transfer fluids. Therefore, an optimization should be done with preference to economic consideration.

8. Material Selections for the Storage System

The material selection also depends on the properties of the ionic liquids, such as corrosive properties, thermal expansive coefficient, and viscosity.

Investigations of the chemical interaction between the ionic liquids and the applied materials such as concrete,

steel, cast iron, stainless steel, copper, and Teflon are in progress. Thermodynamic properties for materials such as activity and electrode potential in liquid have significant effects on their application properties (Gokcen and Reddy, 1995). Accelerated testing methods such as high temperature, high pressure, and electrochemical corrosion techniques will be used for the study.

CONCLUSIONS

Based on the experimental results and above discussion, following conclusions were obtained.

- (1) Ionic liquids have excellent technical properties for the applications as liquid thermal storage media and heat transfer fluids. The properties include high heat capacity, wide liquid temperature range, and high density.
- (2) Other properties of ionic liquids also contribute to the qualification of ionic liquids as liquid thermal storage media and heat transfer fluids, such as high chemical stability, non-volatility, high heat capacity, and high storage density.
- (3) For C_8mimPF_6 ionic liquid, the storage density is 378 MJ/m^3 and liquid temperature range is from -75 to 416°C .
- (4) Low viscosity and high thermal conductivity make ionic liquids excellent candidates as heat transfer fluids for solar thermal power plant system.
- (5) Economic feasibility of ionic liquids as liquid thermal storage media and heat transfer fluids needs to be further investigated.

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