Assessment of thermal and transport properties of ionic liquids as suitable absorbent for absorption cooling applications

H M Ariyadi¹, S Yamaguchi¹ and K Saito¹

¹Department of Applied Mechanics and Aerospace Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Email: hifni.ariyadi@aoni.waseda.jp

Abstract. Ionic liquids, salts which have liquid phase at temperature below 100ºC, have been widely introduced in engineering applications, including absorption cooling systems. The application of ionic liquids in absorption cooling systems is intended to remove the disadvantages of conventional working fluids such as corrosion and crystallization. In terms of thermodynamic performances, theoretical investigation based on solubility behavior of ionic liquids in natural refrigerants show a competitive performance in comparison with conventional working fluid. Nevertheless, heat transfer performance, which is also an important key in absorption cooling systems, particularly in terms of system design and size, needs to be deeply explored and investigated. This study aims to assess the thermal and transport properties of ionic liquids as absorbent in relation to the heat and mass transfer characteristics of these working fluids. The thermal and transport properties of ionic liquids proposed as absorbent for absorption cooling systems are collected, and heat and mass transfer characteristic of these ionic liquids based on their thermal and transport properties are investigated and analyzed. Finally, the most suitable ionic liquids for absorption machines, both in terms of thermodynamics and heat and mass transfer performances can be proposed.

1. Introduction
Absorption cooling systems are recently getting more attention and consideration with the rapid economic growth and increase of energy demand. This is due to the fact that these systems can be driven with wide variety of renewable energy such as solar energy, geothermal, and even waste heat to produce cold thus carries a primary energy saving, and emission reduction. Moreover, absorption systems contain non-CFC and therefore, environmentally friendly and becomes a competitive alternative to conventional vapor compression cooling systems. Similar to vapor compression cycle, absorption cycle is based on the cooling and heating process associated with phase changes of evaporation and condensation of refrigerant fluid at different temperature and pressure levels.

One of the most common working fluid pair in absorption cooling systems is water/LiBr. In this working pair, water works as refrigerant and aqueous LiBr solution works as absorbent. The water/LiBr absorption cycle is used mainly for cooling and heating purpose as it cannot produce cold below 0°C. Being natural fluids, both are emission free and ozone friendly resulting with zero global warming potential (GWP) and ozone depletion potential (ODP). However, the applications of absorption cycle working with water/LiBr are limited by corrosion and crystallization problems. Many attempts have been addressed to eliminate abovementioned drawbacks, such as proposing multicomponent salts solution absorbent [1], adding surfactants and additives [2], and proposing novel absorbent such as ionic liquids (IL) [3]. The latter application in absorption cooling systems can eliminate the abovementioned drawbacks as ionic liquids have liquid phase in wide range of temperature, negligible vapor pressure, non-corrosive, non-toxic, highly soluble with most of natural refrigerant, and thermally stable [3]. In addition, the thermophysical properties of ionic liquids can be adjusted by combining the cation and anion pair [4].
Studies on the use of water/ionic liquid working pairs as working fluid for absorption cooling applications are growing in number. Recent studies on the cycle performance of absorption cooling systems using water/ionic liquid working pairs have been published in many literatures, proposing some ionic liquids as new absorbent for water refrigerant such as 1,3-dimethylimidazolium dimethylphosphate ([dmim] [DMP]), 1-ethyl-3-methyl- imidazolium dimethylphosphate ([emim] [DMP]), 1-ethyl-3-methylimidazolium ethylsulfate ([emim] [EtSO₄]), etc. Based on theoretical thermodynamic calculation using vapor-liquid equilibrium data, the coefficient of performance and solution circulation ratio of single-stage absorption cooling systems using water/ionic liquid fluids is quite competitive in comparison with conventional water/LiBr working fluid [5] considering the above-mentioned advantages of ionic liquids over conventional aqueous LiBr solution.

In fact, the performances and efficiencies of an absorption system are not only determined by coefficient of performance and solution circulation ratio, but also determined by system design and size, initial cost and the operating cost of the machine, which are strongly dependent on the working fluid properties. Selecting and proposing a new working fluid for this system therefore should be carried out properly, considering not only solubility property of refrigerant in the absorbent, but also transport properties of the working fluid mixtures which influence the heat and mass transfer performance, such as viscosity, thermal conductivity, and diffusion coefficient.

Although studies on the cycle performance of absorption cooling systems using water/ionic liquid working pairs have been performed by many researchers, the assessment of thermal and transport properties of these new working pair remains incomplete. This study aims to assess the thermal and transport properties of ionic liquids as absorbent in order to obtain the suitable ionic liquids with optimum heat and mass transfer performance, which is an important parameter in absorption cooling systems, particularly in terms of system design and size.

2. Methodology

In this paper, two ionic liquids, namely 1-ethyl-3-methyl imidazolium ethyl sulfate [emim] [EtSO₄] and 1.3-dimethyl imidazolium dimethyl phosphate [dmim] [DMP] are selected as absorbent for water refrigerant. Thermal and transport properties and vapor-liquid equilibria of water/ [dmim] [DMP] mixtures necessary for the simulation are obtained from NIST database [6]. In addition, to obtain the diffusion coefficient of water in ionic liquid, a general correlation is used, as suggested by Krannich et al. [7]. The thermal and transport properties of coolant water and water vapor are calculated using correlation of IAPWS95 Revision 2016 [8].

The assessment of the properties is done in two parts. The first part is modelling the vapor liquid equilibria to build the pressure-temperature-composition (PTX) diagram. The PTX charts then can be used to estimates the specific operative conditions of the absorber based on operative conditions of the systems. From the first parts, the values of most important properties of selected working fluids can be obtained, compared, and analysed. And finally, the heat and mass transfer characteristics of the working fluids in an absorber can be evaluated using simple model.

Heat and mass transfer characteristics of ionic liquid based working fluid in the absorber is evaluated using a model constructed from energy and mass balance equations, derived from the absorption process takes place in an infinitesimal area of the tube as schematically shown in Fig. 1. Detail of mathematical description of the model can be found in [9].

The absorbent-refrigerant solution enters from the top of the tube, downwards through the inner wall as a falling film. In addition, the water vapour enters from the top of the vertical tube and be absorbed by the ionic liquid solution. The solution leaves the absorber through the bottom of the tube as less concentrated in salt than at the entrance.

The cooling water flows from the bottom of the absorber through tube annulus space to remove the heat of absorption. The heat is transferred from the solution to the cooling water while mass transfer process occurs in the vapor-solution surface.
Figure 1. The schematic diagram of water vapor absorption process in vertical tube falling film absorber.

Assuming that the vapor-solution interface is in saturated condition and the bulk solution is perfectly mixed along the tube, the water vapor absorbed by the solution can be calculated using following equation

\[
\frac{dm}{dz} = k_s (\pi D_i) (c_{H_2O_{out}} - c_{H_2O})
\]  

(1)

Moreover, with assumptions that the heat transfer only occurs in horizontal direction, and there is no heat loss in the absorber, from the energy balance at the solution side, the solution temperature at a control volume can be written as follows

\[
\frac{dT_s}{dz} = \frac{H_v - \Delta H_{S,S}}{m_s C_{P_s}} \frac{dm}{dz} + \frac{U n D_i (T_s - T_c)}{m_s C_{P_s}}
\]  

(2)

Similarly, the cooling water temperature at a control volume can be written as follows

\[
\frac{dT_c}{dz} = \frac{U n D_i (T_s - T_c)}{m_c C_{P_c}}
\]  

(3)

3. Results and Discussions

3.1. Properties Comparison

In this subsection, thermos-physical and chemical properties of water/ionic liquid mixtures is discussed. The comparison is analysed under typical operative conditions of absorber, both in inlet and outlet. This consideration is taken because absorber plays as the most important component in the system which affects the overall performance of the systems.

**Solubility.** In absorption technologies, solubility of refrigerant in the absorbent is one of the most important properties that may reflects the performance of the systems. The coefficient of performance of an absorption cooling cycle can be roughly estimated from the solubility behaviour in a Dühning
diagram plot. To be a good working pair for absorption application, the refrigerant must be well soluble in the absorbent under the conditions in which absorption takes place. High solubility and affinity of refrigerant in the absorbent reduce the amount of absorbent needed to circulate the refrigerant at certain cooling capacity, thus decreasing pumping power and reducing heat exchangers size.

Solubility of water in [dmim] [DMP] and [emim] [EtSO₄] have been measured and well correlated using Non-Random Two-Liquids (NRTL) model by He et al. [10] and Wang et al. [11]. PTX diagrams of water in [dmim] [DMP] and [emim] [EtSO₄] mixtures are presented in Fig 2 (a) and (b), respectively. Although they concluded that both solutions show significant negative deviation to ideal Raoult’s law, in term of mass concentration these two ionic liquids show considerably lower solubility than LiBr salt.

**Figure 2.** PTX diagram of water/[dmim][DMP] (a) and water/[emim][EtSO₄] (b)

PTX diagrams in Fig 2 show that at the same operation conditions working fluid mixtures with wide concentration line distribution have more refrigerant mass concentration in absorber-generator loop in comparison with working fluid mixtures with narrow concentration line. Therefore, the working fluid mixtures with wide concentration line distribution have lower solution flow rates than the fluid mixtures with narrow concentration line distribution, as it has higher concentration difference between strong and weak solution.

Apart of concentration distribution line, the solubility of water in [dmim][DMP] is much better than in [emim][EtSO₄], with the fact that the amount of water in water/[dmim][DMP] solution at a certain temperature and pressure is much higher than in water/[emim][EtSO₄]. An example of the concentration (both weak and strong solution) of studied ionic liquid in comparison with LiBr solution at different typical operative conditions ($T_{abs}=T_{cond}=30~40$ °C, $T_{evap}=5~10$ °C, $T_{gen}=80~90$ °C) is summarized in Table 1.

| $T_{evap}$ (°C) | $T_{abs} = 30$ °C | $T_{abs} = 40$ °C |
|----------------|------------------|------------------|
| [dmim][DMP]    | [emim][EtSO₄]   | LiBr             |
| 5              | 52.57            | 68.83            | 96.14            | 57.81            |
| 8              | 50.76            | 50.57            | 64.55            | 95.27            | 56.08            |
| 10             | 48.46            | 49.13            | 64.55            | 94.58            | 54.90            |

Table 1. Saturation absorbent concentration at various operative conditions

$T_{gen}$ Solution concentration leaving the generator (% mass of absorbent)
3.1.1. Dynamic viscosity

One of the most common issue in ionic liquids that may reduce their potential as absorbent is their high viscosity. High viscosity of absorbent can cause significant pressure drops in the solution circulation loop, which can result in increase of pumping power or larger system size. He et al. [10] and Bhattacharjee et al. [12] have determined and correlated the viscosity of water/[dmim][DMP] and water/[emim][EtSO₄] solutions, respectively.

![Figure 3](image)

**Figure 3.** Viscosity (a) and density (b) of water/ionic liquid mixtures at saturation condition ($T_{evap}=5$ °C) and different absorber temperature

Fig 3 (a) shows viscosity of water/ionic liquid mixtures at saturation condition ($T_{evap}=5$ °C) and different absorber temperature. As it can be observed from Fig. 3 (a), the dynamic viscosity of water/[emim][EtSO₄] is the highest in comparison with water/[dmim][DMP] and conventional fluid water/LiBr. An interesting point is that at temperature lower than 30 °C, the viscosity of water/[dmim][DMP] is lower than water/LiBr.

3.1.2. Density

The density of water/ [dmim][DMP] and water/[emim][EtSO₄] have been measured by He et al. [10] and Bhattacharjee et al. [12]. The density of water/ionic liquid mixtures at saturation condition ($T_{evap}=5$ °C) and different absorber temperature is shown in Fig 3 (b) with the density of water/[emim][EtSO₄] is almost similar with water/[dmim][DMP], and the density conventional fluid water/LiBr is much higher than other two mixtures. With lower density, the pumping power necessary to transport the solution from the low-pressure system to the high-pressure system can be reduce.

3.1.3. Heat capacity

Heat capacity is also one of the most important properties used to evaluate the thermal load and heat transfer characteristic of each components and thermal performance (COP) of the whole systems. Several experimental data of heat capacity of the studied working fluids have been published in literatures [10, 13].
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Fig 4 shows the heat capacity of studied solutions at typical entrance absorber conditions at various degree of subcooling. The solution concentration is determined from a condition than the solution is saturated when leaving the generator at temperature of 90 °C and pressure of 4.25 kPa (corresponds to \( T_{\text{cond}} = 30 \) °C). This condition is used to plot the heat capacity over absorber temperature as the heat transfer phenomena in the absorption process starts at the entrance of absorber. The correlation based on experimental data shows that the heat capacity of aqueous ionic liquid solutions is higher than that of water/LiBr solution, being that of water/\([\text{dmim}][\text{DMP}]\) is the highest (see Fig 4 (a)).

3.1.4. Mass diffusivity

Mass diffusivity is an important property to evaluate mass transfer characteristic particularly in the absorber. Although this property is important, to the best of our knowledge there is no available data or correlation of mass diffusivity of water in studied ionic liquids and thus, to estimate the mass diffusivity of water in ionic liquids a method suggested by Krannich et al. [7] is applied.

Using similar condition to Fig 4 (a), the mass diffusivity of water in studied solutions at typical entrance absorber conditions at various degree of subcooling is then plotted in Fig 4 (b). In this figure, it shows that the mass diffusivity of studied ionic liquids is much lower in comparison with conventional aqueous LiBr solution, being \([\text{emim}][\text{EtSO}_4]\) is the lowest among three studied working fluids. This low mass diffusivity will significantly affect to the mass transfer behaviour, as will be discussed later.

3.2. Heat and Mass Transfer Characteristics

In order to get more understanding on the relation of properties assessment of ionic liquid based absorbents on the performance of the absorption process, heat and mass transfer characteristics of absorption process of water vapor in ionic liquid solutions is theoretically studied, using absorber configuration and operation conditions similar to the one studied by Ariyadi et al. [14]. Mass flux and mass flux in water/\([\text{dmim}][\text{DMP}]\) and water/\([\text{emim}][\text{EtSO}_4]\) working fluids in comparison with conventional water/LiBr working fluid are shown in Fig. 5 (a) and (b), respectively, within solution Reynolds number varies up to 400. Fig. 4 shows that the mass flux of all studied working fluids increases with the increase of solution Reynolds number until reaches its peak then decreases with the increase of solution Reynolds number. This is because at low solution Reynolds number (i.e. \( \text{Res} < 20 \) in the case of \([\text{dmim}][\text{DMP}]\)) absorption process tends to be more dominant than heat transfer process, thus the absorption mass flux increases with the increase of solution Reynolds number. At higher solution Reynolds number heat transfer process is more dominant than absorption process, thus the absorption mass flux decreases with the increase of solution Reynolds number. In general, the mass
flux and its optimum values trends follow an order of water/LiBr > water/[dmim][DMP] > water/[emim][EtSO₄], because the mass flux is affected by diffusivity and the solubility of water in the absorbent. The low solution Reynolds number, where the optimum mass flux is reached, is affected by the high viscosity of water/ionic liquid solutions.

![Figure 5](image)

**Figure 5.** Mass flux (a) and heat flux (b) vs solution Reynolds number of water/LiBr and water/ionic liquid solutions.

Although mass flux of water/[dmim][DMP] solution is lower than that of water/LiBr solution, at the same absorber configuration and operation conditions, the heat flux of that water/[dmim][DMP] working fluid is slightly higher than that of water/LiBr working fluid due to higher heat capacity of water/[dmim][DMP] solution (see Fig. 5 (b)). The heat flux of that water/[emim][EtSO₄] working fluid remain the lowest as its low heat capacity and low heat of absorption.

### 4. Conclusions

Thermophysical and transport properties of ionic liquids absorbent for water refrigerant has been assessed at typical operative conditions both in inlet and exit of an absorber, together with theoretical studies on the heat and mass transfer characteristics of absorption process in a vertical tube absorber. The performances of a refrigerant/absorbent working pairs do not only depend on the vapor-liquid equilibrium or solubility, but is also affected by its thermophysical and transport properties. Among studied ionic liquids, in general, [dmim][DMP] provides better properties than [emim][EtSO₄]. Although, [dmim][DMP] still has undesirable properties that can make significance decrease in the system performance, such as low solubility and diffusivity, and high viscosity, this ionic liquid provides better properties, such as high heat capacity, low density, and no solidification risk in comparison with conventional water/LiBr solution which can make this ionic liquid as better alternative absorbent to LiBr solution. In theory, the thermophysical properties of ionic liquids can be adjusted by combining the cation and anion pair. However, in practice, tuning ionic liquids to have good properties for absorption application is not an easy task. Considering the high potential application of ionic liquids as an absorbent in absorption application, further study on other ionic liquids which have better properties for absorption cooling applications remains necessary.

### Nomenclature

| Symbol | Definition |
|--------|------------|
| c      | concentration |
| $C_p$  | constant pressure heat capacity (J/kg K) |
| $D_i$  | inside diameter (m) |
| $H$    | enthalpy (J/kg) |
| $k$    | mass transfer coefficient (m/s) |

### Subscript

| Subscript | Meaning |
|-----------|---------|
| abs       | absorber |
| c         | cooling water |
| cond      | condenser |
| evap      | evaporator |
L tube length (m)  gen generator
m mass flowrate (kg/s)  H2O water
P pressure (kPa)  int vapor-solution interface
Re Reynolds number  s solution
T temperature (°C)  sub subcooled
U overall heat transfer coefficient (W/m² K)  v vapor
X solution concentration (% mass of absorbent)

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