

Ionic Liquids as Sorption Cooling Media

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ABSTRACT

Today one of the major challenges in industry and society is the development of energy efficient processes and applications resulting in a sustainable treatment of our environment. Almost all industrial processes produce large amounts of waste heat which could not be used for any further purposes. Since approximately 100 years there has been a lot of research done to make this energy accessible. One approach is the use of sorption techniques to transfer the “poor” waste heat into useful “rich” heat or cooling. The breakthrough is still not achieved due to the lag of efficient, non-corrosive, non-toxic and fully miscible working solutions with a sufficient to good Coefficient of Performance (COP).

Ionic liquids as a relatively new class of substances – salts that are liquid at temperatures below 100°C – offer innovative opportunities as absorbent fluids in sorption systems. In cooperation with the institute of technical thermodynamic Karlsruhe (ITTK) we have investigated their application for the use in sorption cooling devices.

Keywords: sorption cooling, ionic liquids, binary mixtures

1 INTRODUCTION

The sorption cooling technology is known approximately since 100 year and a lot of research has been done on this field. There are a lot of advantages of this technique compared to common compression cooling systems. The major difference and advantage is the type of the used energy for cooling. In compression cooling systems high quality electrical energy is consumed to produce cold. With the sorption technique instead heat could be transformed directly into chill. By using this principle, it would be possible to transform waste heat, e.g. from industrial processes, or solar thermal heat into useful energetically rich cooling. Nevertheless, this technology has still not achieved wider breakthrough, since efficient, non-corrosive, non-toxic working pairs that finally have to have a reasonable Coefficient of performance are not identified. Only for niche application, where a noisy compressor has to be avoided, e.g. fridges for caravans

(running with gas) or in hotel rooms, sorption cooling systems are used already. In industry sorption cooling is mostly used to produce cold water from waste heat. Today’s state of the art sorption cooling systems are based on the working pairs Ammonia/water or LiBr/water. In the latter case, there are already some drawbacks: First of all the salt could crystallize in the device leading at least to an expensive service revision or sometimes also to irreparable damages of the cooling device system. In addition, the salt is very corrosive and toxic leading to high demands on safety and stability of the applied materials. Therefore alternative working pairs are needed.

Ionic Liquids (ILs) are a comparable new class of materials, consisting entirely of ions, which are liquid at unusual low temperatures.¹⁻² Typical structural motifs combine organic cations with inorganic, or, more rarely, organic anions (Figure 1). The lower symmetry of the cations and/or anions as well as the delocalization of the charge over larger parts of the ions by resonance, are mainly responsible for the low melting points of ionic liquids. The manifold combinations of cations and anions provide a large number of liquid materials with (tunable), often unique properties such as high conductivity, high thermal and electrochemical stability, negligible vapor pressure and non-flammability. In addition, the ionic liquids are less or even non-corrosive and could be designed as hydrophobic or hydrophilic to be miscible with a broad range of different solvents. These properties making them to ideal candidates as media in sorption cooling systems.³⁻⁶

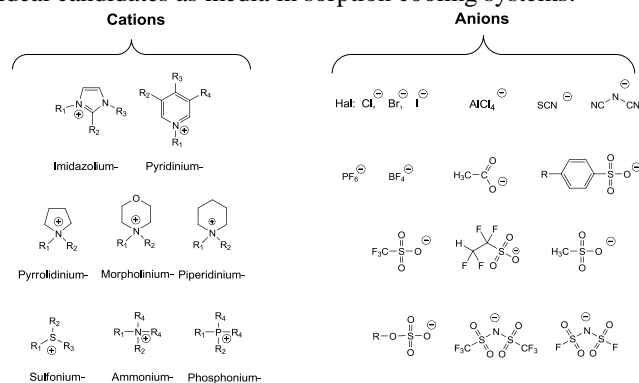


Figure 1: Examples of typical cations and anions.

2 RESULTS AND DISCUSSTION

2.1 Working principle of a sorption cooling device.

The schematic overview of a sorption cooling system is given in Figure 2. The device contains four different working sections: the evaporator, the absorber, the generator and the condenser. In the evaporator the cooling fluid water is evaporated into the gas phase at reduced pressure. The energy is delivered by an external water circulation leading to a decrease in temperature of the water in the circulation. This cold water (9 °C-16 °C) could then be used to cool external devices. Since the evaporation process will stop as soon as the gaseous phase is saturated with the cooling fluid the gas must be removed from the process. Therefore the gas is transferred into the absorber where the absorbent (ionic liquid) is present. The ionic liquid has a strong affinity to the cooling fluid leading to absorption of the gaseous fluid and removal from the gas phase. To recover the saturated sorption media, the working pair mixture is transferred to the generator. An external heat source (in this case hot water 60 °C- 90 °C) delivers the necessary energy to evaporate the working fluid again from the sorption media. The source for the needed energy could be waste heat from external industrial processes. The recovered absorbent is then transferred back to the absorber. The gaseous cooling media instead is feed into the condenser and liquefied again. To close the sorption cooling circle the cooling media is transferred via a throttle valve to the evaporator. The cooling capacity is given by $\zeta = \dot{Q}_0 / \dot{Q}_H$ whereas \dot{Q}_0 is the delivered chill and \dot{Q}_H the used heat in the generator.

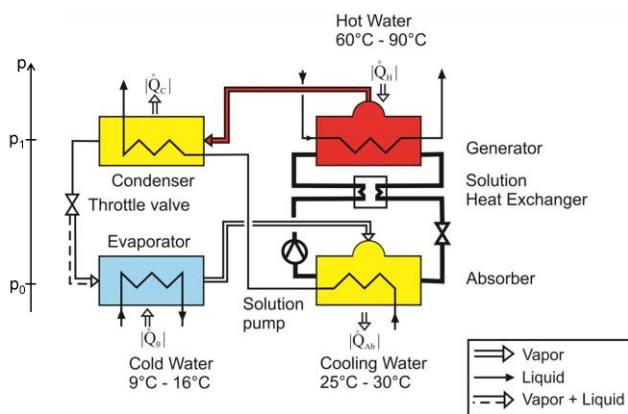


Figure 2: Schematic overview of a sorption cooling system

2.2 Selection of suitable working pairs.

The used working pairs for the sorption cooling system must fit to some framework requirements. The refrigerant should have a high enthalpy of evaporation and must be completely miscible with the adsorbents (ionic liquid) combined with an enhanced vapor pressure degradation. In addition, the adsorbents should have a vapor pressure as

low as possible. The absorbents should be thermal stable up to 150°C and non-corrosive. Regarding environmental and safety aspects the used media should also be non-toxic, bio degradable and non-explosive.

Those requirements led to the preselection of 10 different ionic liquids. The investigated liquids are shown in Figure 3. The chosen ionic liquids are all soluble in water and containing different classes of anions namely lactate, sulfonate, glycolate, acetate, mesylate, hydrogensulfate, nitrate, formiate and chloride.

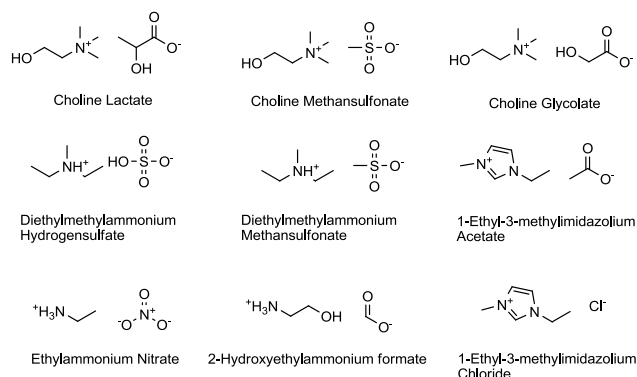


Figure 3: Possible ionic liquids as sorption media.

The identified ionic liquids were investigated regarding their vapor-liquid equilibrium data, viscosity, thermal stability and corrosivity.

2.3 Physical-chemical measurements

To get some information about the suitability of a possible working pair ionic liquid/water some thermodynamic data are needed about the behavior of the applied mixture. Therefore the measurement of the vapor-liquid equilibrium is necessary. With that information in hand it is possible to determine the degassing width ($\Delta\xi$) of the systems indicating the difference between concentrations of the refrigerant media in the media rich ionic liquid of the absorber (ξ_r) and the media poor ionic liquid of the generator (ξ_a).

$$\Delta\xi = \xi_r - \xi_a \quad (1)$$

The vapor-liquid equilibrium (VLE) measurements of the different ionic liquids were conducted in a dynamic measurement apparatus shown in Figure 4. It consists of a glass flask with an internal volume of 0.5 l as equilibrium cell, a circulation pump, and a Fourier transform infrared (FTIR) spectrometer. The equilibrium cell is equipped with a demister to prevent liquid droplets to get into the spectrometer. The liquid phase was heated by a water thermostat and the temperature was measured by a platinum resistance thermometer (PT 100 sensor). The temperature of the whole apparatus, except the spectrometer itself and the feed line, was equal to the equilibrium temperature.

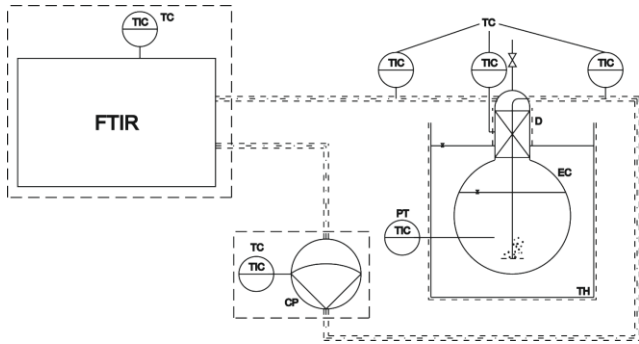


Figure 4: Dynamic VLE measurement cell: TH, water thermostat; EC, equilibrium cell; D, demister; TC, thermocouple; TIC, temperature-control of the six different sections; PT, platinum resistance thermometer; CP, circulation pump; FTIR, Fourier transform infrared spectrometer.

The measured activities of water in ionic liquids and Lithium Bromide are summarized in Figure 5. This plot of water activity ($a_w = p_w/p_{ws}$) vs. mass fraction of water (w_w) has the advantage that the degassing width ($\Delta\xi$) of the different working pairs could be quickly estimated from the slope of the plotted curves. The slopes of the novel media are in the same range as the common used LiBr resulting in akin degassing width suggesting similar performance characteristics for an application in a sorption cooling device.⁷⁻⁸

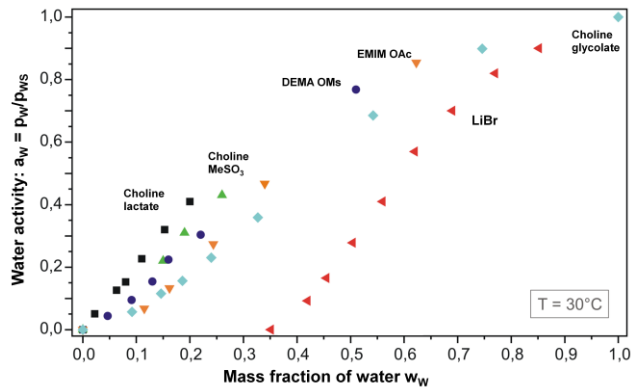


Figure 5: water activity vs. mass fraction of water in different ionic liquids and Lithium Bromide.

The dynamic viscosities of the ionic liquids with various water contents were determined at different temperatures.⁷⁻⁸ Exemplarily the measurements for Diethylmethylammonium Methanesulfonate (DEMA OMs) are shown in Figure 6. This diagram displays as expected that the viscosity of the ionic liquid decreases with increasing water content. In this context it has to be stressed, that viscosity is an important factor for the applicability of sorption media to cooling devices, since a high viscosity would lead to higher energy costs for pumping the media and furthermore to a lower heat transfer in the device due to the lower

wettability of the heat exchanger. The ionic liquid of choice should therefore have a low viscosity already in neat form with ideally a viscosity similar to water.

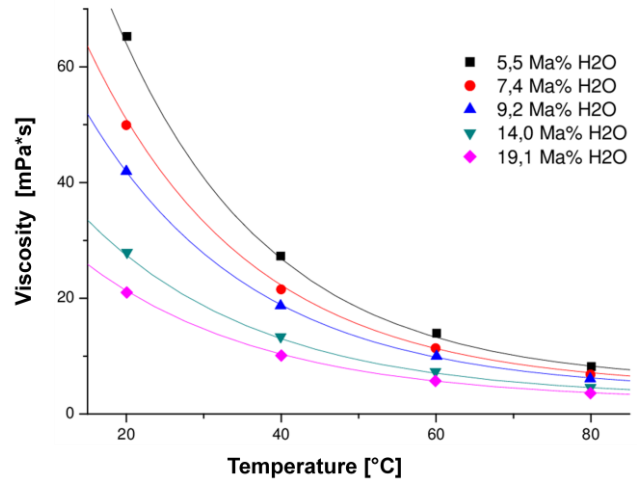


Figure 6: Viscosity of Diethylmethylammonium Methanesulfonate with different mass% of water.

2.4 Suitability of the suggested ionic liquids

All the measurements of the different suggested ionic liquids were compared concerning their suitability as sorption media and graded. The results are summarized in the Table 1 below.

Table 1: Rating of ionic liquids as sorption media

Ionic Liquid	Rating	Remark
Choline lactate	-	$\Delta\xi$ too small
Choline methanesulfonate	-	$\Delta\xi$ too small high viscosity
Choline glycolate	++	
1-Ethyl-3-methyl imidazolium acetate	+	halide content (corrosivity)
Diethylmethylammonium methanesulfonate	++	
Diethylmethylammonium hydrogensulfate	-	$\Delta\xi$ too small high viscosity
Ethylammonium nitrate	+	
2-Hydroxyethylammonium formiate	+	
1-Ethyl-3-methylimidazolium chloride	(+)	halide content (corrosivity)

After evaluation of the results Diethylmethylammonium methanesulfonate was identified as one suitable candidate for testing in a pilot sorption cooling device and produced in larger quantities.

2.5 Pilot sorption cooling device

A pilot sorption cooling system was set up and modified by the Karlsruher Institut of Technology using a common LiBr/water sorption cooling device by SK Sonnenklima. A picture of the modified device is shown in Figure 7.



Figure 7: Pilot sorption cooling device

In first test runs with Diethylmethylammonium methanesulfonate a minimum cold water outlet temperature of 11°C was achieved with this device ($\dot{Q}_0/\dot{Q}_H = 0.48$). The cooling capacity was 1.51 kW on average. The small capacity resulted mostly from the limited heat transfer in absorber and generator since ionic liquid/water systems are more viscous than common LiBr/water systems. This combined with insufficient wettability of only 32% of the pipe bundle heat-exchangers decreases the performance drastically. To enhance the heat transfer new concepts for an improved heat exchanger were developed. The wettability of the used pipe bundle heat-exchanger could be increased by simply covering the pipes with a steal net. The more efficient wettability was already demonstrated in laboratory tests and is illustrated in Figure 8. Currently a second generation sorption cooling device is under construction with improved setup concepts and more suitable working materials.

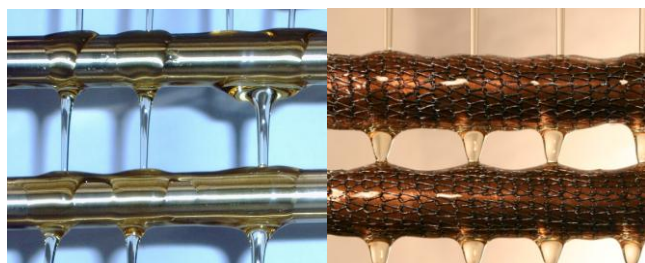


Figure 8: Pipe bundle in a heat exchanger: common setup (left) improved setup with covering net (right).

3 SUMMARY

We have investigated several water soluble ionic liquids regarding their applicability as sorption media for sorption cooling systems. After evaluation of viscosity, thermal stability, vapor-liquid equilibrium of the different ionic liquids, Diethylmethylammonium methanesulfonate was chosen as candidate for a sorption cooling test device. First test devices clearly delivered a proof of concept for the replacement of LiBr/water with ionic liquid/water as working media. But the efficiency of the common system was not achieved and optimized device setup and working conditions are necessary. A second generation device is currently built and first tests are running.

Acknowledgment

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