# IONIC LIQUIDS AS NEW ABSORBENTS FOR ABSORPTION CHILLERS AND HEAT PUMPS

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**Abstract:** In this paper, ionic liquids are proposed as new absorbents for absorption chillers and heat pumps. The theoretical and experimental based research of Technische Universität Berlin, Bavarian Center for Applied Energy Research (ZAE Bayern) and Graz University of Technology is presented and test and simulation results are discussed. The results show the suitability and promising potential of ionic liquids as absorbents but the research organizations agree in the need of further effort in R&D.

**Key Words: ionic liquids, absorption chiller, absorption heat pump**

## 1 INTRODUCTION

Up to the 1980s many different working pairs for absorption chillers have been proposed. Later, only few research groups investigated new absorption working pairs. This is because the prevalent working pairs water/LiBr and ammonia/water meet the existing requirements of common applications quite well. Water/LiBr is used for air-conditioning and $NH_3$/water mainly for refrigeration.

Nowadays, applications with further requirements have been discussed as there are high medium temperature level (solar cooling in hot climate, heat pump use in retrofit applications) and high driving temperature level (high efficient triple-effect chillers, heat transformers for industrial applications). This required a reanimation of research activities regarding new working pairs to overcome the drawbacks of the prevalent working pairs. LiBr solution runs the risk of crystallization at high temperature lift and the corrosion problem becomes grave at high driving temperatures. The drawback of ammonia/water systems is the remarkably increasing pressure with higher medium temperature level. This is problematic on the one hand regarding construction issues and on the other regarding pump energy consumption.

In the last few years, ionic liquids (ILs) - organic salts composed entirely of ions which remain liquid at or close to ambient temperature - have been discussed as absorbents capable to replace LiBr solution as they do not have the crystallization risk and they are potentially less corrosive.

## 2 RESEARCH AT TU BERLIN

In 2008, the Technische Universität (TU) Berlin and the company Evonik Industries AG started a public funded project (German Federal Ministry of Economics and Technology by grant no. 0327472A and B) to evaluate the potential of ionic liquids as new absorbents for absorption chillers (Kühn et al. 2009, Seiler et al. 2010, Schneider et al. 2011). In the course of the project Evonik produced several customized ionic liquids which have been tested in a small scale absorption chiller prototype with glass shell at the TU Berlin (see Figure 1).

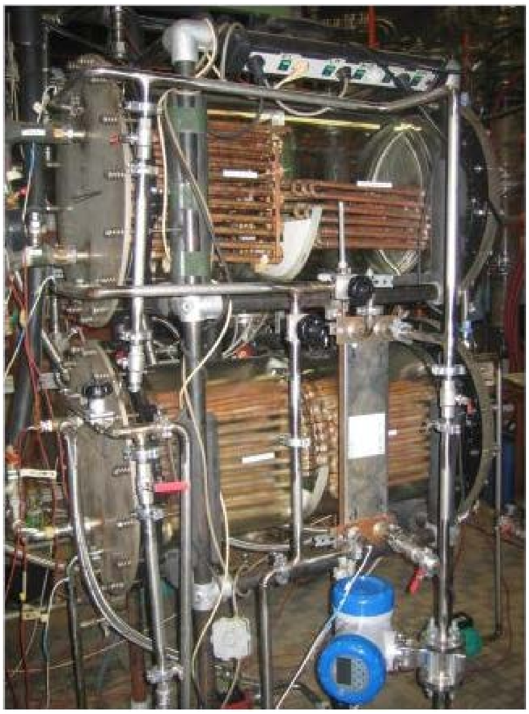
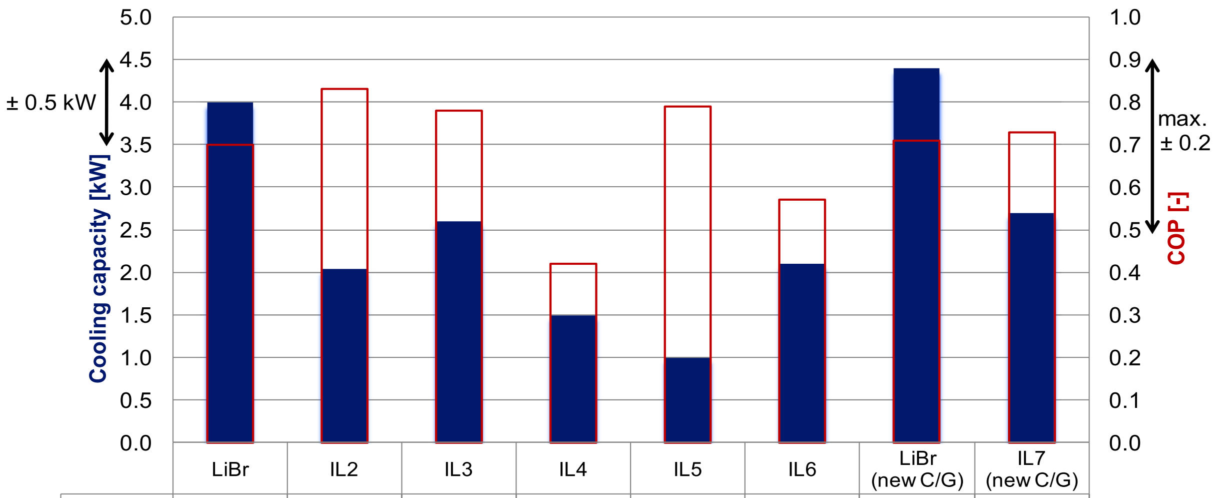


**Figure 1: Photograph of the test rig at TU Berlin**

The best tested ILs showed the same efficiency (COP) as the water/LiBr system and a cooling capacity (Q_E) representing 80% of the cooling capacity of a water/LiBr system without additives (65% of a water/LiBr system with 2-ethyl-1-hexanol additive, see Figure 2). The tests presented in Figure 2 have been carried out with 75°C driving temperature, 27°C cooling water temperature and 18°C chilled water inlet temperature. Due to the higher viscosity of the ILs a more powerful solution pump has been installed after testing IL3 in order to achieve a solution flow rate (V_Sd) of 100 l/h or more for ILs, too. The test of IL7 has been carried out after the installation of a new condenser (C) and a new generator (G) heat exchanger with slightly other dimensions. Therefore, this test results must be compared to the appropriate LiBr test results (previous column). The analysis of different influencing parameters indicated that the reduced cooling capacity results from a mass transfer inhibition probably due the higher average solution concentration during operation.




| | LiBr | IL2 | IL3 | IL4 | IL5 | IL6 | LiBr (new C/G) | IL7 (new C/G) |
|---|---|---|---|---|---|---|---|---|
| ■Q_E [kW] | 4.0 | 2.0 | 2.6 | 1.5 | 1.0 | 2.1 | 4.4 | 2.7 |
| □COP [-] | 0.70 | 0.83 | 0.78 | 0.42 | 0.79 | 0.57 | 0.71 | 0.73 |
| V_Sd [l/h] | 100 | 70 | 65 | 100 | 100 | 100 | 100 | 100 |
| m_Sd [g/s] | 40 | 18 | 17 | 30 | 33 | 31 | 44 | 32 |

**Figure 2: Test results of water/LiBr and water/IL working pairs (Kühn et al. 2012)**

Nevertheless, the potential of ionic liquids as absorbents for absorption chillers and heat pumps has been shown. It has been experimentally demonstrated that the tested ionic liquids allow a depression of the water partial pressure in the same order of magnitude as LiBr solution, but in most cases at higher salt concentrations. It has also been demonstrated that they do not crystallize at temperatures above 20°C and that a stable operation over a wide range of driving, heat sink and heat source temperatures is possible. The use of ionic liquids in absorption chillers and heat pumps appears to be possible under conditions at which LiBr solution runs the risk of crystallization. Heat sink temperatures up to 60°C have been tested without crystallization of the IL. Additionally, potential advantages by using adiabate absorption have been studied. First experiments using a spray dispersion test rig have been carried out.

## 3 RESEARCH AT ZAE BAYERN

To investigate the suitability of ionic liquids - especially 1-ethyl-3-methylimidazolium ethyl sulfate – as sorbent at the Bavarian Center for Applied Energy Research (ZAE Bayern) an experimental absorption chiller was built. Due to the expected properties of ionic liquids, particularly high viscosity and surface tension, generator and absorber of the system were built as spray chambers with external plate heat exchangers (see Figure 3). This optimizes the heat and mass transfer, since both processes are separated and the wetting of a tube bundle heat exchanger is not further required.

The measurements show the general feasibility. Thermally driven chillers can run and supply chilling capacity with an ionic liquid as sorbent. While operated with EMIM $EtSO_4$ the experimental plant reached a lower specific capacity per volume compared to commercial systems based on $H_2O$/LiBr and using tube bundle heat exchangers (LT2, LT10, LT52, suninverse), see Figure 4 (Radspieler and Schweigler 2011).

**Figure 3: Photograph of the test rig at ZAE Bayern**

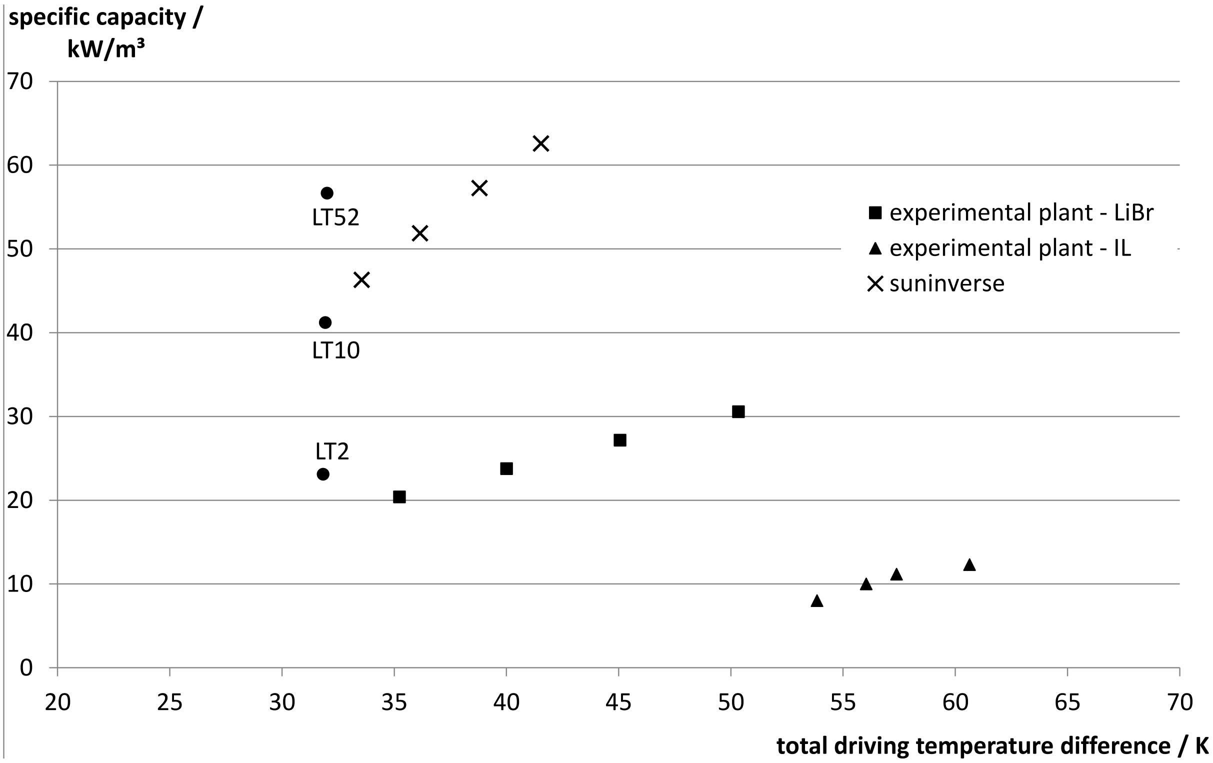



**Figure 4: Comparison of capacity (IL and LiBr)**

Figure 4 shows the capacities of the test rig operated with LiBr and IL compared to commercial chillers (suninverse and three different chiller of Thermax ltd.) During the experiments a reaction between the refrigerant (water) and the ionic liquid was observed. Due to the decreased capacity and the lack of chemical stability further efforts are needed to find a suitable combination of working fluid and applied process.

## 4 RESEARCH AT TU GRAZ

A single-stage absorption heat pump (AHP) process with working mixtures of ammonia as the refrigerant and ionic liquids as the absorbent were investigated at TU Graz by means of thermodynamic simulations using the software program ASPEN Plus (Kotenko et al. 2011). From the literature the following binary mixtures of $NH_3$/IL were found: $NH_3$/[bmim][$BF_4$], $NH_3$/[bmim][$PF_6$], $NH_3$/[emim][$EtSO_4$] and $NH_3$/[emim][$TF_2N$] (Yokozeki und Shiflett 2007a;b). Thermodynamic simulations of the investigated $NH_3$/IL AHP-processes at TU Graz have shown that their efficiencies at certain boundary conditions are higher than those of a conventional $NH_3/H_2O$ AHP. However, the COP of the investigated $NH_3$/IL AHP-processes decreases more in comparison with a conventional $NH_3/H_2O$ AHP when the temperature lift increases. The reason for that is a low difference between the $NH_3$ mass concentration in the rich and poor solution and therefore a high solution flow rate.

The "best" simulation results have been obtained for the AHP-process using the working mixture $NH_3$/[bmim][$PF_6$] (see Figure 5). It is more efficient than a conventional $NH_3/H_2O$ AHP at absorber / evaporator outlet temperatures $t_{ABS\_OUT}$ / $t_{EVA\_OUT}$ of 25/5°C and 35/5°C if the generator outlet temperature $t_{GEN\_OUT}$ is higher than ca. 75°C and ca. 115°C respectively.

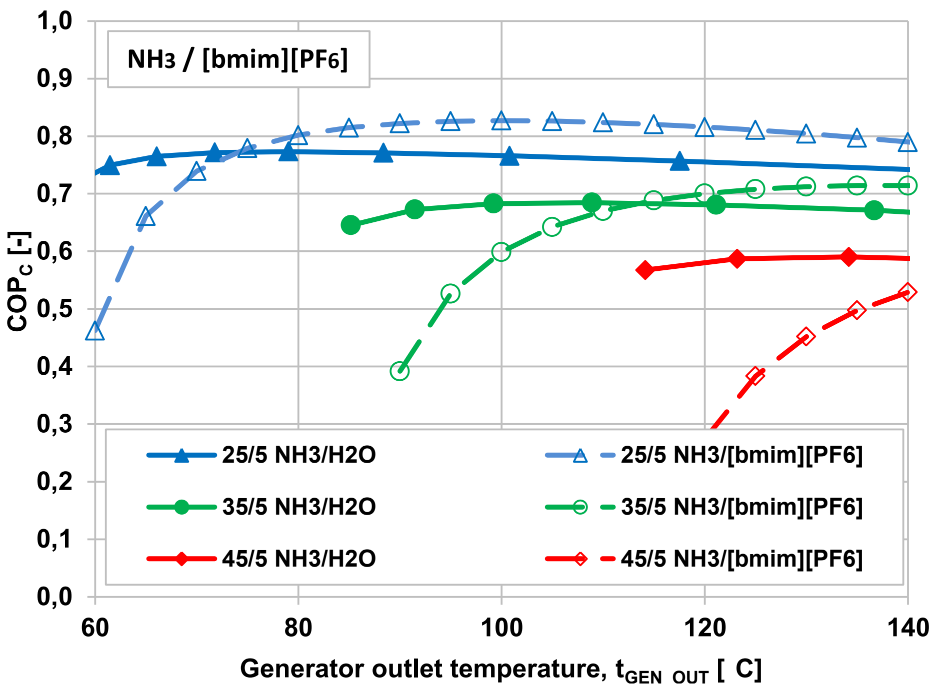



**Figure 5: Simulation results of the COP for $t_{ABS\_OUT}/t_{EVA\_OUT}$=25/5°C, 35/5°C and 45/5°C of $NH_3$/[bmim][$PF_6$] AHP-processes without rectification column in comparison to a conventional $NH_3/H_2O$ AHP-process with rectification column depending on $t_{GEN\_OUT}$**

In general, it was concluded that the following are consequences caused by ILs instead of $H_2O$ with $NH_3$ as refrigerant:

- the rectification column is not necessary;
- the ratio of the required solution pump power demand to the generator heating capacity increases significantly;
- the required capacity of the solution heat exchanger increases as well and has stronger influence on the process COP.

As the next step in the research of $NH_3$/IL AHP-processes experimental investigations are necessary.

## 5 SUMMARY

At TU Berlin seven ionic liquids tailor-made by Evonik Industries AG have been tested as absorbents for water in a small scale absorption chiller. At ZAE Bayern tests with water and 1-ethyl-3-methylimidazolium ethyl sulfate have been carried out using a test rig with adiabatic absorption and desorption. At TU Graz simulations have been performed using ammonia as refrigerant and ionic liquids as absorbents. The results show the suitability and promising potential of ionic liquids as absorbents for absorption cooling machines and heat pumps. The possibility to tailor the properties according to the requirements described is intriguing. More tests are required, but a competitive IL-based working pair seems to be possible in the near future.

## 6 NOMENCLATURE

| | |
|---|---|
| *[bmim][$BF_4$]* | 1-butyl-3-methylimidazolium tetrafluoroborate |
| *[bmim][$PF_6$]* | 1-butyl-3-methylimidazolium hexafluorophosphate |
| *[emim][$EtSO_4$]* | 1-ethyl-3-methylimidazolium ethylsulfate |
| *[emim][$TF_2N$]* | 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide |

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