# A REVIEW ON ABSORPTION HEAT PUMPS AND CHILLERS USING IONIC LIQUIDS AS ABSORBENTS

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**Introduction:** Absorption heat pumps and chillers are thermally activated systems that use heat, instead of an electrical driven system (compressor), to produce chilled water for air conditioning and refrigeration applications. They are widely acknowledged as a prospective candidate for efficient and economic use of solar energy, waste heat recovery methods for cooling and heating applications. The conventional working fluid (absorbent + refrigerant) combinations used in these systems include lithium bromide + water (LiBr + $H_2O$) and water + ammonia ($H_2O$ + $NH_3$) where LiBr and $H_2O$ are the absorbents, respectively. These conventional working pairs are characterized by some drawbacks such as low (sub-atmospheric) operating pressure, crystallization and corrosion for LiBr + $H_2O$ system and low system performance, need for rectification process of the refrigerant stream and high driving heat source temperature for $H_2O$ + $NH_3$ system. In order to overcome these drawbacks of the conventional working pairs and to extend the operating range of absorption systems for different boundary conditions, various mixtures of natural refrigerants such as ammonia ($NH_3$), carbon dioxide ($CO_2$) and water ($H_2O$) with Ionic Liquids (ILs) have been researched for absorption heat pump and chiller processes over years [1-22].

The objective of this paper is to present a review of the scientific literature on absorption heat pumps and chillers working with ILs and natural refrigerants ($NH_3$, $H_2O$ and $CO_2$). It highlights both theoretical and experimental work done by several researchers on this topic, as well as on the literature survey for the thermodynamic property models used for the prediction and correlation of thermodynamic properties.

**Discussion:** We have discussed the performance of ILs as new absorbents in absorption systems based on system performance parameters such as energy efficiency (COP), solution circulation flow ratio (*f*), cooling/heating capacity and temperature lift. The influence of the working fluid mixture on the performance and application/working range of the absorption systems under different operating conditions are also discussed.

**For heat pumps and chillers with ILs + NH3:** The performance of a single-effect absorption cycle using [bmim][$BF_4$], [bmim][$PF_6$], [emim][$EtSO_4$] and [emim][$TF_2N$] as absorbents for $NH_3$ are studied in the literature [5]. A comparison with the conventional absorbent ($H_2O$) was also investigated for the same cycle configuration at different cycle operating conditions. In the reviewed paper it has been found that the dependency of COP on the operating conditions varied for different IL absorbents for the same refrigerant. According to Kotenko et al. [5], for some ILs and operating conditions the COPs can be higher than the values for the conventional $NH_3$+$H_2O$ mixture, but these COPs values decreases significantly more when the temperature lift increases in comparison with the conventional mixture. The best simulation in terms of the COP corresponds to the working mixture $NH_3$+[bmim][$PF_6$].

**For heat pumps and chillers with ILs + H2O:** The functional capability of replacing LiBr by ILs as absorbent for $H_2O$ in absorption heat pumps and chillers has been demonstrated using theoretical absorption cycle analysis as well as in few experimental works [2,6-9]. Yokozeki and Shiflett [2] used twelve ILs with $H_2O$ in a simple cycle configuration analysis using COP and *f* as comparing parameters, which explains the efficiency and compactness of the system. In the analysis [mmim][$(CH_3)_2PO_4$] and [emim][$(CH_3)_2PO_4$] show the best results, with the highest COP and lowest *f* values. The COP result was about 85-88% that of the water+LiBr system. The results of cycle simulations indicate that IL + $H_2O$ system could be competitive with $H_2O$ + LiBr system particularly for optimized ILs.

**For heat pumps and chillers with ILs + $CO_2$:** A few absorption refrigeration system analyses are available in the literature. Martin and Bermejo [20] reported that the process with ILs has a lower COP than $H_2O$ + $NH_3$ and $H_2O$ + LiBr systems due to necessity of operating with a higher solution flow rate. However, near-optimum performance is obtained in a wide range of process conditions.

**Summary:** The absorption cycle, mainly single-effect, analysis found in the literature indicates that COP of the absorption heat pumps and chillers with the adequate ILs can be similar to the COP of the conventional working pairs. But, other advantages like low driving temperature, high temperature lift, compact size, low initial cost (no rectifier cost) and no corrosion can be brought to the system by using ILs which make ILs interesting novel absorbent for natural refrigerants. The correctness of the cycle analysis is highly dependent on the accuracy of the thermodynamic properties of working mixture. Activity coefficient and equation of state (such as cubic and PC-SAFT) models are used so far mainly for the property modelling of working fluid mixtures with ILs. The viscosity and wetting performance of ILs influences the heat and mass transfer in the absorber and desorber/generator which highly influences the cooling/heating capacity of the absorption system.

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## References:

1. A. Yokozeki, Theoretical performances of various refrigerant–absorbent pairs in a vapor-absorption refrigeration cycle by the use of equations of state, *Applied Energy* 80 (2005) 383–399.
2. A. Yokozeki and M.B. Shiflett, Water solubility in ionic liquids and application to absorption cycles, *Ind. Eng. Chem. Res.* 49(2010) 9496-9503.
3. A. Yokozeki and M.B. Shiflett, Vapour-liquid equilibria of ammonia + ionic liquid mixtures, *Applied Energy* 84 (2007) 1258-1273.

4. L.E. Ficke, Thermodynamic properties of imindazolium and phosphonium based ionic liquid mixtures with water or carbon dioxide. *PhD Dissertation University of Notre Dame, Indiana*, April, 2010.
5. O. Kotenko, H.Moser and R. Rieberer, Thermodynamic analysis of ammonia/Ionic Liquid absorption heat pumping processes, *ISHPC*, Padova, Italy, April 6-8, 2011.
6. X. Zhang, D. Hu, Performance simulation of the absorption chiller using water and Ionic Liquid1-ethyl-3-methylimidazolium dimethylphosphate as the working pair, *Applied Thermal Engineering* 31 (2011) 3316-3321.
7. C. Romich, N. Merkel, K. Schaber, T. Schubert and M. Koch, A comparison between lithium bromide-water and ionic liquid-water as working solution for absorption refrigeration cycles, *23rd IRC,* Prague, Czech Republic, August 21-26, 2011.
8. A. Kuhn, O. Buchin, M. Seiler, P. Schwab and F. Ziegler, Ionic liquids-a promising solution for solar absorption chillers?, *3rd Solar air-conditioning conference,* Palermo, Sicily, Italy, September 30th – October 2nd , 2009.
9. M. Radpieler and C. Scweigler, Experimental investigation of ionic liquid EMIM EtSO4 as solvent in a single effect cycle with adiabatic absorption and desorption, *ISHPC*, Padova, Italy, April 6-8, 2011.
10. B. Shelide, Study of ionic liquid applications in absorption refrigeration*, Report; University of Notre Dame*, 2006.
11. A. Yokozeki and M.B. Shiflett, Absorption cycle utilizing ionic liquid as working fluid*, International Publication Number WO 2006/084262*, 2006.
12. W.Cai, M. Sen, and S. Paolucci, Dynamic modeling of an absorption refrigeration system using Ionic Liquids, *Proceedings of ASME International Mechanical Engineering Congress and Exposition*, Seattle, Washington, USA, November 11-15, 2007.
13. P.Wasserscheid and M.Seiler, Leveraging Gigawatt potentials by smart heat-pump technologies using ionic liquids, *ChemSusChem* 2011, 4, 459 – 463.
14. M. Radpieler and C. Scweigler, Experimental investigation of ionic liquid EMIM EtSO4 as solvent in a single effect cycle with adiabatic absorption and desorption*, ISHPC, Padova, Italy,* April 6-8, 2011.
15. MC Schneider and M Seiler, Sustainable energy supply by absorption chillers and heat pumps using multifunctional working pairs, *Chemie Ingenieur Technik* 2011, 83, No. 9, 1502–1509.
16. M. Seiler, P. Schwab and F. Ziegler, Sorption systems using Ionic Liquids, *International Sorption Heat Pump Conference*, *Seoul, Korea,* September 23-26, 2008.
17. M.C. Schneider, R. Schneirder, O. Zehnacker, U. Buchen, F. Cudok, A. Kühn, T. Meyer, F. Ziegler and M. Seiler, Ionic liquids: new high-performance working fluids for absorption chillers and heat pumps*, ISHPC,* Padova, Italy, April 6-8, 2011.
18. A. Yokozeki and B.M. Shiflett, Ammonia solubilities in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* 46(2007) 1605-1610.
19. M. Sen and S. Paolucci, Using carbon dioxide and ionic liquids for absorption refrigeration, *7th IIR Gustav Lorentzen Conference on Natural Working Fluids*, Trondheim, Norway, May 28-31, 2006.
20. A. Martin and M.D Bermejo, Thermodynamic analysis of absorption refrigeration cycles using ionic liquid + supercritical $CO_2$ pairs, *J. of Supercritical Fluids* 2010, 55, 852-859.

21. A. Boesman and T. J.S. Schubert, Novel pairs of working substances for absorption heat pumps, absorption refrigeration machines and heat transformers, *International Publication Number 2008/0028777AL*, 2008.
22. G. Zuo, Z. Zhao, S. Yan and X. Zhang, Thermodynamic properties of a new working pair: 1-Ethyl-3-methylimidazolium, *Chemical Engineering Journal* 156 (2010) 613–617.