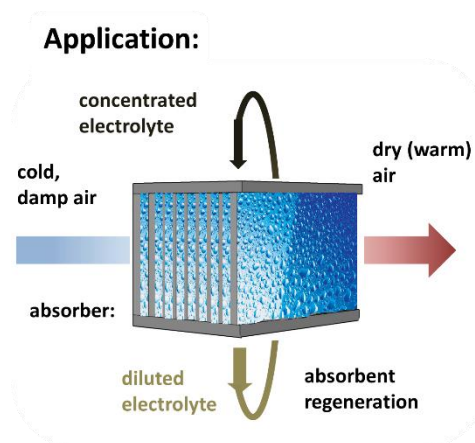


Analyzing the solution behavior of hygroscopic Imidazolium and Choline based ILs for optimizing liquid sorption media.

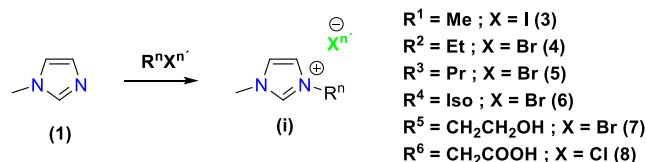
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Abstract:

Absorption storage systems in combination with solar thermal systems are a potential attempt for the reduction of greenhouse gases.¹ The currently used sorption media like LiCl or LiBr show problems concerning crystallization, corrosion or low storage capacity.^{2, 3} Imidazolium and Choline based ILs in combination with organic anions may be an alternative to the classical hygroscopic salt solutions, because they are able to quickly absorb large amounts of water in an exothermic process. To optimize the sorption system we have screened the latter device parameters, especially the solution behavior of the ILs to determine structure-property relationships and improve the performance. Therefore, a calorimetric analysis offers an insight in the interaction between cation, anion and water.⁴ In combination with other investigation, we hope to obtain a simulation of the sorption process.



Synthesis:



Scheme 1

One of the main aspects when searching new working fluids for open absorption storage systems is a low corrosivity, which is a problem by the currently used electrolytes. Furthermore, the viscosity, the surface tension and the diffusion are important parameters and have an influence of the performance of the system. For the use in our systems, it is necessary to have liquid media, which can be pumped and preferably does not crystallize during regeneration. As a result, especially RTILs are an interesting approach to avoid this problem. The known requirements reduce the possible anions mainly to the organic ones, esp. formate, acetate, lactate and oxalate. It is understandable, that the choice of the cations results from the same considerations as for the anions. This means a relative short alkyl chain length or hydrophilic groups like alcohols or carboxylic acids attached to the 3-position in 1-methylimidazole (**Scheme 1**).

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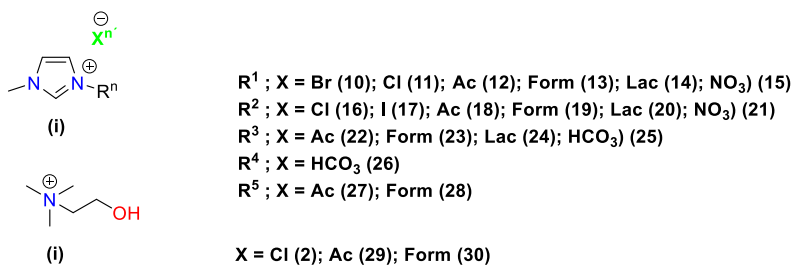


Chart 1

The first step to synthesize the ILs is an quaternization reaction to the imidazolium salt.⁵⁻¹¹ Subsequently the anion can be changed by an ion exchange column according to Alcalde et al. (**Chart 1**).¹² To verify the completeness of the exchange we analyzed the NMR Spectra and perform a silver test. The high purity of these procedure is evidenced by the crystal structures of the compounds **3, 7, 8, 12, 13, 19, 25-30**.⁴

Thermodynamic measurements:

Due to the main application, the investigated ILs should release a large amount of heat in relation to the absorbed amount of water. This heat can be divided in two parts: the condensation energy, which is fixed, and the dilution energy. To measure the heat of dilution, an isothermal titration calorimeter was used. This allows an accurate analysis of the dilution process. The measurements are plotted in the **diagram 1** and show the potential of the ILs to rise up the performance in comparison to conventional salts. On the one hand, the liquid aggregate state allows to operate over a very wide concentration range without the risk of crystallization. On the other hand, the dilution process produces considerably more energy compared to our benchmark LiCl, which is also investigated.

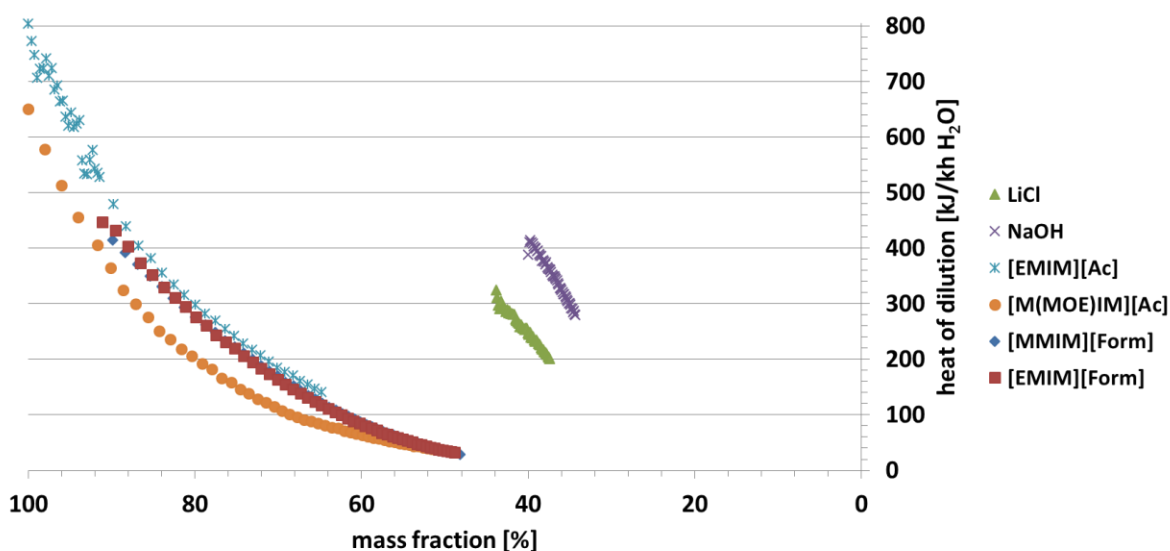


Diagram 1

Structure property relationship:

To identify suitable sorbents, structure property relationships are an important tool. In our investigations, we analyzed the [MMIM]- and the [EMIM]-cation. In order to determine the interactions between the cation and anion in the solid state, several crystalline ILs were analyzed (two examples in **figure 1**). With these crystal structures the Hirshfeld surfaces of the anions could be calculated and give us the possibility to calculate the volume of the anion. From the graphs (**Diagram 2**), it is clearly visible that not only the size of the anion, but also its nature influences the heats of dilution. When considering the heat of dilution in relation to the lattice energy, there is a large gap between the inorganic and organic anions. The dilution energy by the chosen concentration of 55 mol/L decreased nearly linear for the four inorganic anions. In contrast to the inorganic anions, the organic provide a much larger heat of dilution although the size is nearly the same. An explanation of this behavior can be found in the smaller interaction between anion and cation as well because of a stronger interaction between anion and water. The trend of the released heats for the [MMIM] and the [EMIM] cation are almost identical. In both cases, the acetate species renders a larger heat of dilution compared with the corresponding formate, even though it has a smaller ionic radius, and thus a higher effective charge.

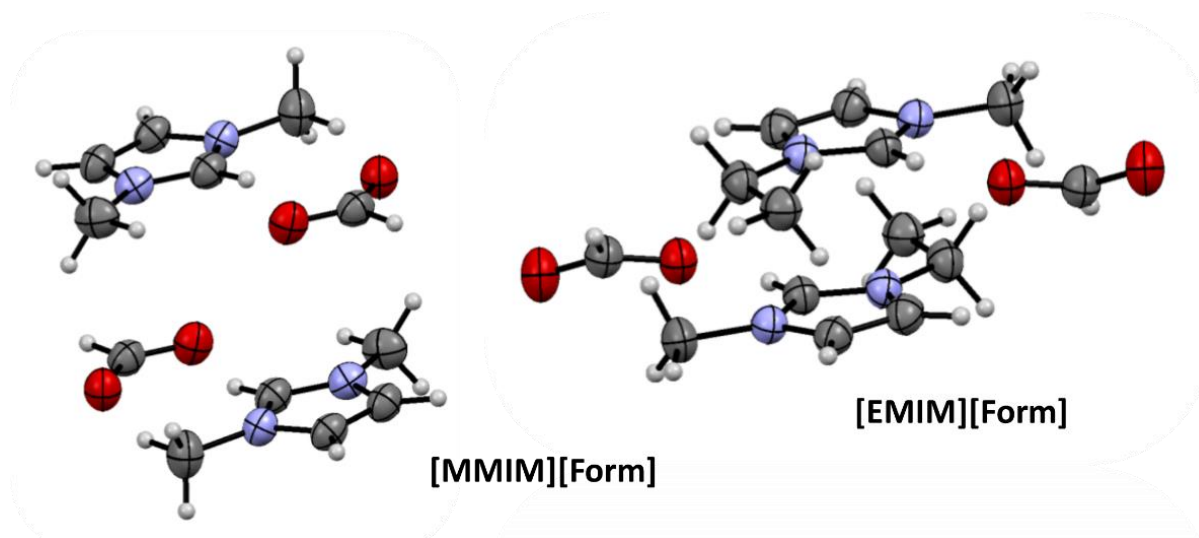


Figure 1

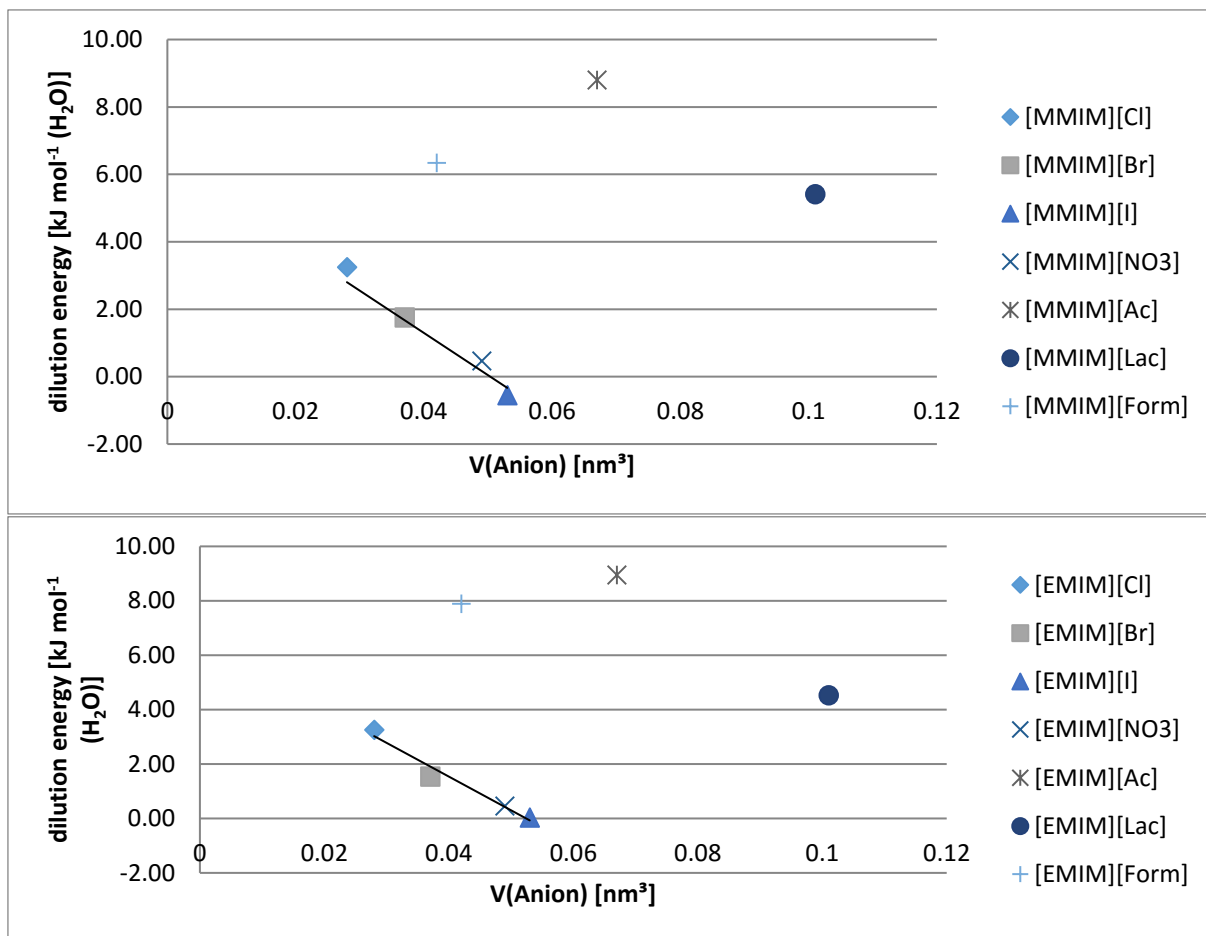


Diagram 2

Conclusion:

In conclusion, with the help of the X-ray diffraction we have analyzed the molecular structures of several ILs (two examples presented) and calculated the molecular volume by the Hirshfeld surface. With an ITC the dilution energy could be determined and together with the calculated anion sizes, an trend could be observed. In addition the investigation of the dilution process of the organic anions show, that the [EMIM][Ac] releases the highest dilution energy. This fact could be explained by the interaction of cation, anion and water. These results show the possibility to use ILs in thermal energy storage systems, because of their benefits compared to conventional salts and the benchmark LiCl.

Acknowledgements:

Financial support by the BMBF project OpenSorp (T.B.). Moreover we are grateful to Prof. U. Jordan for helpful discussions.

Literature:

1. C. Janiak and S. K. Henninger, *Nachr. Chem.*, 2013, **61**, 520-523.
2. P. Wasserscheid and M. Seiler, *ChemSusChem*, 2011, **4**, 459-463.
3. M. Uerdingen, C. Treber, M. Balsler, G. Schmitt and C. Werner, *Green Chem*, 2005, **7**, 321-325.
4. T. Brünig, K. Krekić, C. Bruhn and R. Pietschnig, *Chem. Eur. J.*, 2016, **22**, 16200-16212.
5. E. M. B. Brian L. Benac and Anthony J. Arduengo, III, *Org. Synth.*, 1986, **64**, 92.
6. S. Jana, A. Parthiban and C. L. L. Chai, *Chem. Commun.*, 2010, **46**, 1488-1490.
7. Z. Fei, W. H. Ang, D. Zhao, R. Scopelliti, E. E. Zvereva, S. A. Katsyuba and P. J. Dyson, *J. Phys. Chem. B*, 2007, **111**, 10095-10108.
8. F. F. D. Oliveira, M. R. dos Santos, P. M. Lalli, E. M. Schmidt, P. Bakuzis, A. A. M. Lapis, A. L. Monteiro, M. N. Eberlin and B. A. D. Neto, *J. Org. Chem.*, 2011, **76**, 10140-10147.
9. Y. Chen, S. Li, Z. Xue, M. Hao and T. Mu, *J. Mol. Struct.*, 2015, **1079**, 120-129.
10. T. Takamuku, Y. Kyoshoin, T. Shimomura, S. Kittaka and T. Yamaguchi, *J. Phys. Chem. B*, 2009, **113**, 10817-10824.
11. L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *PCCP*, 2001, **3**, 5192-5200.
12. E. Alcalde, I. Dinarès, A. Ibáñez and N. Mesquida, *Molecules (Basel, Switzerland)*, 2012, **17**, 4007-4027.