Ionic Liquids as Heat Transfer Medium

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ABSTRACT

Heat transfer media are of great importance for many industrial processes in which heat needs to be transported or transformed. Ionic liquids possess a couple of unique features that allow the development of new highly specialized applications. The combination of very low vapor pressure, good heat capacity and high thermal stability allows the use of ionic liquids as heat transfer media at very low pressures or under vacuum.

Keywords: ionic liquid, thermal fluids, heat capacity, heat transfer

1 INTRODUCTION

Ionic liquids are defined as pure salts with melting points below 100°C. This unusual character is caused by the lower symmetry and the charge distribution over the molecule. These remarkable compounds have made their way from laboratory curiosities to functional fluids for a wide range of applications. While in the beginning ionic liquids were mostly regarded as alternative "green" solvents for catalysis they are now used in many different applications such as energy conversion, energy storage, lubricants, electrolytes, solvents, or analytical applications.^[1-4]

2 IONIC LIQUIDS AS THERMAL FLUIDS

Their high heat capacity, low vapor and incombustibly make them to promising candidates as thermal fluids. A limiting factor thereby is the resistance to thermal decomposition. Many ILs are misleadingly reported in the literature to be stable to high temperatures.^[5] In case of short-term heating, there are ionic liquids which are stable up to 400°C. However, the major challenge is to create fluids with a long-term thermal stability.

The goal of one of a present government-funded project (Federal Ministry of Education and Research, BMBF, Germany) is to develop a concept for short term chemical storage of volatility resulting electrical energy through photovoltaics and wind by fixing of CO_2 . A suitable

chemical energy source with high energy density is Methane. The project idea can be simplified as follows:

• Excess of electrical energy from renewable resources is used for the cleavage of water into Hydrogen and Oxygen

 $2 \operatorname{H}_2 O(\mathbf{l}) \rightarrow 2 \operatorname{H}_2(\mathbf{g}) + O_2(\mathbf{g})$

 $\Delta_R H^0 = +286 \text{ kJ/mol}$

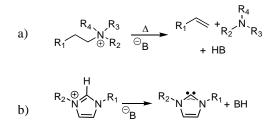
• On demand Hydrogen is used to react with waste CO₂ to form methane

 $CO_2(g) + 4 H_2(g) \rightarrow CH_4(g) + 2 H_2O(g) \quad \varDelta_R H^0 = -165 \text{ kJ/mol}$

- The ionic liquid acts as reaction medium and as well as heat transfer fluid
- Long-term stability of 250°C is required

2.1 Identification of Suitable Ionic Liquids

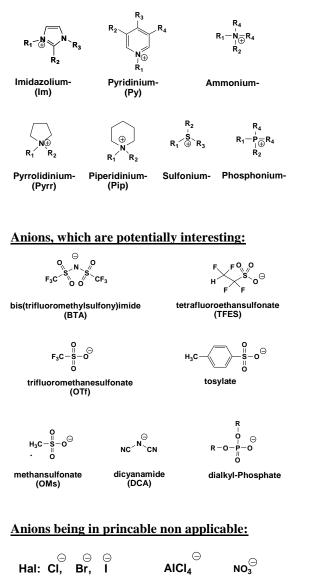
As well as for other applications of ionic liquids, an important point is to utilize the existing variety of options to produce tailor-made compounds. Developing stable ionic liquids requires the prevention of the degradation pathway. For instance, it is known that ammonium-based ionic liquids undergo Hofmann-elimination and imidazoliumbased ionic liquids a deprotonation:

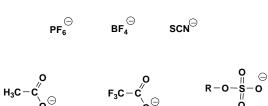


Scheme 1: Hofmann-elimination and deprotonation.

By pre-selecting a comprehensive matrix of different anions and cations from our substance library of more than 600 compounds, using known physical and chemical data from literature and from our data pool, interesting structural motifs were defined.

Cations, which are potentially interesting:









acetate

trifluoroacetate alkyl-Sulfate

Screening of Thermal Stability 2.2

The studies on thermal stability were carried out as shown in Figure 1. Each of ionic liquids were heated one hour at 150, 200, 250 and 300° C in a heating block. The result was documented by recording of digital photographs.



Figure 1: Experimental setup for screening thermal stability.

Evaluation of stability screening tests was made by simple optical description of the samples. ILs were defined as (preliminary) stable for our purpose, if they showed at 250°C no change to a deep black color and no formation a solid. Selected ILs were analyzed by using TGA (Thermogravimetric analysis) at the DVGW-Research Institute (Engler-Bunte-Institute, Karlsruhe Institute of Technology, KIT, Germany).

2.3 Experimental Details for TG-Analysis

The measurements were performed on a Thermo-Microbalance TG 209 F1 Iris[®] from Netzsch Gerätebau GmbH:



At the beginning of each TG experiment, the sample space including the previously filled sample (approximately 10 mg IL) was five times evacuated and purged to remove impurities (e.g. solvent) from the ionic liquids. During the measurement analysis software records the mass change as a function of time. The test period is at least 450 min., and all experiments consists of a heating-up period (at the critical temperature: 1 K/min) and a longer isothermal period (6 h, respectively for 150°C, 200°C, 250°C and 300°C). Selected ionic liquids were measured as described. ILs which remained stable at certain temperature were then analyzed in a further measurement at elevated temperatures. The following diagram demonstratees the stability of a few selected IIs at 250°C:

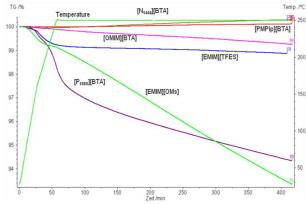


Diagram 1: TG-Analysis of slected ILs.

3 CONCLUSION

By pre-selecting a comprehensive matrix of different anions and cations from our substance library of more than 600 compounds, using known physical and chemical data from literature and from our data pool, we identified in carefully chosen screening tests novel interesting structural motifs. In collaboration with DVGW Research Unit the obtained data were evaluated and the ionic liquids were modified according to the required properties.

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