

2. Objective

Motivated by promising examples of improvements brought forward by the use of ionic liquids in current state of the art research (see chapter 1.4.2) concerning extended solvation properties, improved recyclability of catalysts or altered chemical behavior, was the main focus of this work directed to implement existing cluster structures into organic media by conversion into ionic liquids. The long term goal is to create unprecedented materials with unique properties such as high viscosity, excellent conductivity and thermal stability - interesting for both material science and synthetic processes with potential usage as catalysts, sensor systems or electrochemically active materials.

As nearly any element can be embedded in a polyoxometalate their compound family is already one of the most versatile available. However polyoxometalates as inorganic salts with high crystal lattice energies are faced with low solubility in non-polar organic solvents restricting their application for catalytic reactions in those media. Conversion of crystalline POMs into ionic liquids may overcome this limitation and may just bring polyoxometalate chemistry to its full potential.

POMs dissolved in ionic liquids as solvents can therefore increasingly be found in literature.^[56-58] Such a straight forward approach may suffice for many applications yet be insufficient for others as dissolution of POM salts in ILs always results in the introduction of two additional ionic species (i.e. the cationic part of the POM salt and the anionic part of the IL) which will alter the physical and chemical behavior of the mixture, thus leading to inadvertent effects, particularly at higher POM loadings (see Figure 11 on the next page).

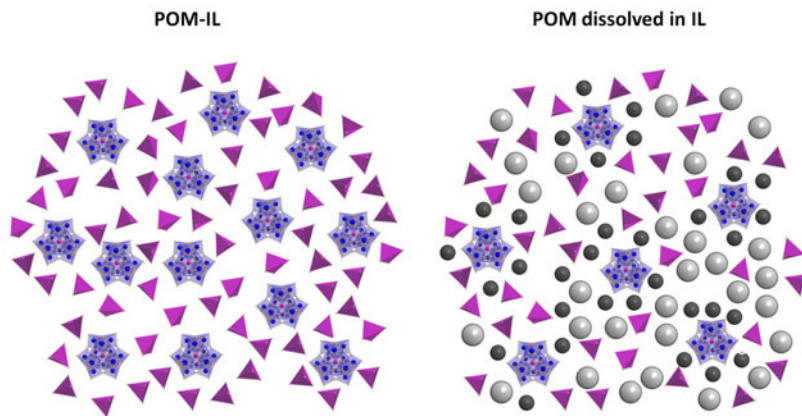


Figure 11 Molecular model for a true POM-IL (*left*) vs. a POM dissolved in IL (*right*). The POM-IL exhibits a much higher cluster density and has less different electrostatic interactions. In a POM-IL only interactions among POMs (blue polyhedra with templating heteroelement in pink) and their charge balancing cations (purple tetrahedra) are possible, whereas for POMs dissolved in a ionic liquid additional interactions with the ionic liquids cations (black balls) and anions (grey balls) occur.

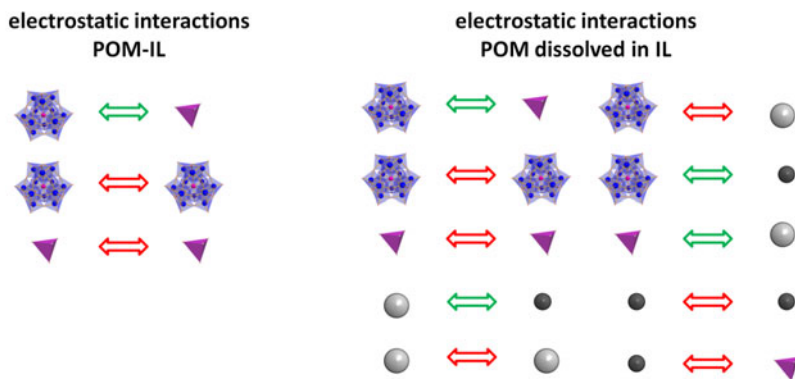


Figure 12 All possible types of electrostatic interactions among the ions of a true POM-IL vs. those of a POM-salt dissolved in IL. Attractive interactions are indicated with a green double arrow, repulsive forces with a red one.

Even if no negative effects arise due to the additional solvent ions and their manifold interaction possibilities (see. Figure 12) is the catalytic activity restricted because dissolution of a POM salt in ILs is limited by solubility. In contrast, true POM-ILs can achieve much higher cluster loadings (as the POM cluster acts as the anionic component

of the IL) being the ideal supported reagent system for the catalyst (in this case the POM) where each molecular unit of the supporting material would bear inherent functionality and be itself free to react.

Therefore the objective of this work and further studies is set to systematically synthesize true polyoxometalate ionic liquids (POM-ILs), to investigate their physiochemical properties and to probe their reactivity fathoming potential applications.

The synthesis of new POM-ILs is supposed to be achieved using sterically demanding cations like tetraalkylammonium, tetraalkylphosphonium or imidazolium ions featuring long alkyl chains. Tunability of the ILs properties is further realized by alternation of the heteroatoms and incorporation of different d-elements into the lacunary site(s) of the mono- or polyvacant cluster anions. Basic characterization of the obtained products is carried out by elemental analysis (EA), infrared spectroscopy (IR) and UV-Vis spectroscopy. Rheological measurements are carried out in cooperation with the LSTM (Lehrstuhl für Strömungsmechanik) to complement the investigation of physical properties of the obtained new ILs.

<http://www.springer.com/978-3-658-08795-1>

New Synthetic Routes to Polyoxometalate Containing
Ionic Liquids

An Investigation of their Properties

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2015, XXI, 122 p. 61 illus., Softcover

ISBN: 978-3-658-08795-1