ABSTRACT

Bartłomiej Gaida

Bio-derived ionic liquids as precursors for sustainable functional materials

Supervisor: Prof Anna Chrobok

Auxiliary supervisor: PhD Alina Brzęczek-Szafran

The main objective of the doctoral dissertation was the research on the synthesis, properties, and applications of ionic liquids derived from sugars and their derivatives. The literature review began with a description of the synthetic pathways for sugar-based ionic liquids. In the following sections, the impact of the structure of selected sugar-based ionic liquids on their properties, such as biodegradability, toxicity, thermal stability, and melting point, was discussed. Finally, a wide range of applications of this group of compounds was presented, covering catalysis, biomedicine, ecology, as well as their use in energy conversion and storage, and biomass dissolution.

In the research section, the synthesis and properties of 19 new carbohydrate-based ionic liquids and salts were described. The studies were divided into three parts depending on the intended applications of the compounds: 1) as phase change materials for renewable energy storage, 2) as precursors for doped carbon materials, and 3) as surface active agents.

Ionic compounds intended for use as phase change materials (PCMs) were synthesized from cations based on derivative of D-glucose or D-mannitol, combined with anions such as Br^-, $[NO_3]^-$, $[OMs]^-$, and $[BF4]^-$. The resulting compounds were characterized for key PCMs properties, including melting point, enthalpy of fusion, decomposition temperature, and thermal stability. The influence of the anions on the recrystallization ability of the synthesized compounds was also analyzed. An important aspect of this part of the study was the examination of hydrogen bonding interactions between cations and anions in the crystal lattice of the obtained compounds. These studies demonstrated that the transformation of carbohydrates into ionic compounds, along with the appropriate selection of anions, can positively affect the recrystallization ability and thermal stability of the resulting compounds.

In the next section, the thermal properties of sugar-based ionic compounds containing anions with cyano groups ($[SCN]^-$, $[DCA]^-$, $[TCM]^-$, and $[TCB]^-$) were examined. These compounds were subjected to pyrolysis to produce doped carbon materials. The influence of the selected anions and carbonization conditions on the morphology, elemental composition, and electrocatalytic properties of the final carbon materials was investigated. As part of the study, a material comparable to the commercial Pt/C catalyst was obtained.

The final chapter of the experimental section was dedicated to sugar-based ionic liquids containing anions known for their surface-active properties ($[DS]^-$, $[C]^-$, and $[DOC]^-$). Critical micelle concentration (CMC) values were determined for the obtained compounds. Additionally, these compounds were applied in the separation of single-walled carbon nanotubes (SWCNTs) using the aqueous two-phase extraction (ATPE) method. The sugar-based surfactants allowed for a better understanding of the role of the cation in the partitioning mechanism via ATPE, and they enabled the development of systems capable of modifying the course of the separation of SWCNTs.