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Azide-alkyne cycloaddition in ionic liquids

AUTHORS
DIANA SLOBODA / UNIVERSITY OF LATVIA, FACULTY OF CHEMISTRY, JELGAVAS 1, RIGA
ANDRIS ZICMANIS / UNIVERSITY OF LATVIA, FACULTY OF CHEMISTRY, JELGAVAS 1, RIGA
EDUARDS BAKIS / UNIVERSITY OF LATVIA, FACULTY OF CHEMISTRY, JELGAVAS 1, RIGA

PURPOSE OF THE ABSTRACT

Ionic liquids (ILs) are low-melting organic salts that are liquid at ambient temperatures. IL solvent properties are easily customizable by changing the IL cation or anion structure. In recent years, supported ionic liquid phase (SILP) technology [1] has been identified as an innovative method for creating custom systems for organic synthesis applications by combining IL with inorganic/organic materials and metal complexes. SILP technology can be explained as IL dispersed with a solvated catalyst on a solid support, creating a porous phase that acts like a catalyst, but the reaction remains homogeneous at the microscopic level. The advantage of such material is that the SILP component is easily removable from reaction media. On the contrary, traditional transition metal catalyst separation from products is often a tedious and resource consuming process that is difficult to scale up, for example, copper catalysts can be removed from products using dialysis against a solution of EDTA followed by water or by filtration on C-18 cartridges.

One of the most recognised transition-metal-catalysed reactions is copper(I)-catalysed azide-alkyne cycloaddition reaction (CuAAC). CuAAC allows a straightforward creation of covalent connections between building blocks via 1,4-triazole linkages. To understand which IL properties would be beneficial for designing a tailored SILP system for CuAAC, we have to first rationalize the azide-alkyne cycloaddition reaction in bulk IL media.

In this work, we studied the benzylazide-phenylacetylene cycloaddition as a model reaction. The uncatalyzed version of the azide-alkyne reaction led to formation of both the 1,4- and 1,5-triazole products; however, the ratio of the regioisomers was found to be solvent dependent. CuAAC in IL media remained selective towards the 1,4-regioisomer. We investigated the impact of IL structure and composition on CuAAC reaction kinetics. The importance of water content in this system is demonstrated by remarkable changes in the reaction kinetic profiles. We tested the effects of coordinating and noncoordinating IL anions on CuAAC reaction kinetics. The influence of the modification of the IL cation structure on CuAAC kinetics is discussed as well. The data obtained from this study are valuable for designing SILP specifically for CuAAC reaction; therefore, improving the efficiency and sustainability of processes where CuAAC is involved.

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FIGURES

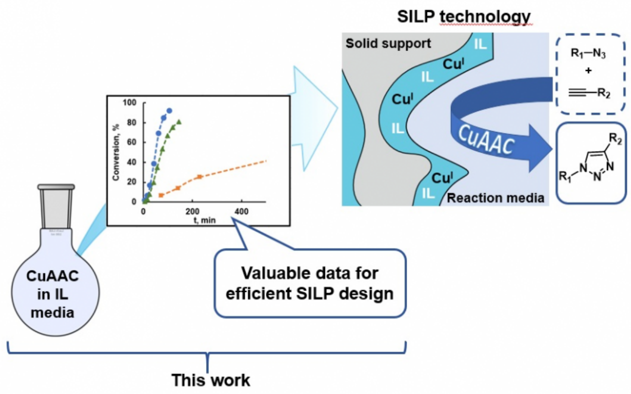

FIGURE 1

Concept of this study

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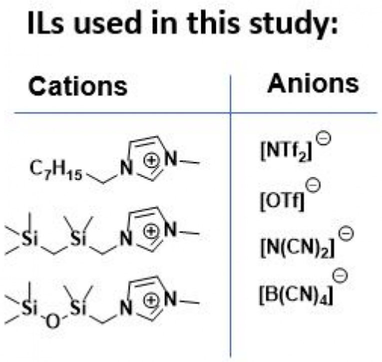

FIGURE 2

ILs used in this study

ILs used in this study

KEYWORDS

Ionic liquids | azide-alkyne cycloaddition | kinetics | triazoles

BIBLIOGRAPHY

[1] Shiflett, M.B. (Ed.) Commercial Applications of Ionic Liquids; Springer: Cham, Switzerland, 2020