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Keys for the Use of Ionic Liquids as Reaction Media in Enzyme-Catalyzed Processes

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Abstract

During recent years there has been a growing interest in the use of ionic liquids as substitutes for organic solvents. That has been due mainly to their unique properties, which highlight their very low volatility. This editorial is focus on analyzing the application of ionic liquids as reaction media in enzyme catalyzed reaction. Specifically, the advantages of using ionic liquids as reaction media for biocatalysts were discussed. Other considerations like green aspect of ionic liquids and the recovery of synthetic products from ionic liquid matrix were also analyzed.

Keywords: Ionic liquid; Biocatalysis; Green chemistry

Introduction

The interest in ionic liquids, often heralded as the green high-tech media of the future, is still increasing rapidly. Ionic liquids (ILs) are organic salts which are liquids under ambient temperature. They consist of an organic cation, and a polyatomic inorganic or organic anion. The structures of common cations and anions of ILs are shown in Figure 1.

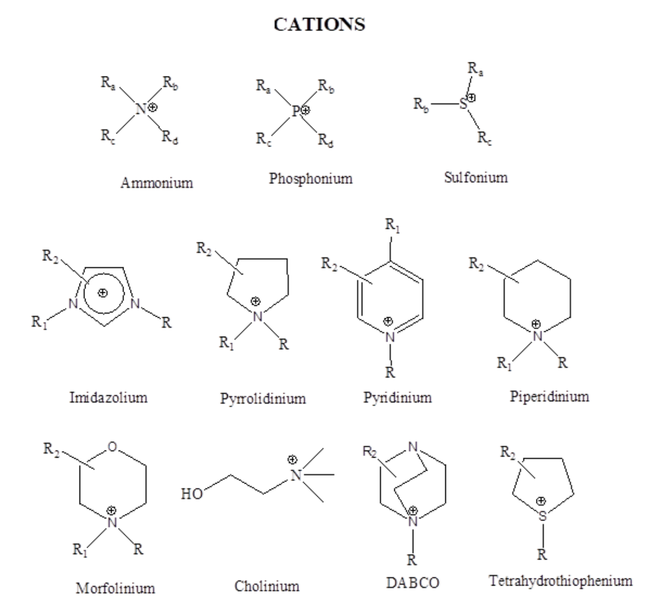

Figure 1: Example of ions involved in ILs.

In addition, to avoiding the use of organic solvents and, thus, the emission of volatile compounds, the use of ionic liquids in enzymology has improved the activity, stability and selectivity of bio catalysis reactions in some cases. Consequently, ionic liquids have emerged as solvents for non-aqueous enzymology [1-6]. Here, we analyzed the keys for using ionic liquids on non-aqueous enzymology in a framework of green chemistry.

The effect of ionic liquids on activity, selectivity and stability of enzymes

Lipases, such as *Candida antarctica* lipase B (CaLB) [7-9], *Pseudomonas cepacia* lipase (PcL) and *Candida rugosa* lipase (CrL) [10,11], have been the most used enzymes in ionic liquids. The ionic liquids have not only been applied in enzymatic reactions catalyzed by lipases but also others enzymes have been used in ionic liquids such as laccases [12-14] and penicillin G acylase [2].

An ionic liquid may play the same role as an organic solvent in affecting the enzyme performance by: (1) stripping off the essential water around the enzyme; (2) penetrating into the microaqueous phase to interact with the enzyme by modifying the protein dynamics, the protein conformation, and/or the enzyme's active site; and (3) interacting with the substrates and products by either reacting with them or by altering their partitioning between the aqueous and nonaqueous phases.

Consequently, the use of ionic liquids could affect positively or negatively the enzyme performance and specifically the enzyme activity, selectivity and stability. De los Ríos et al. [9] studied the effect of ionic liquids on activity, selectivity and stability of *Candida antarctica* lipase B (CaLB) for a trans esterification reaction. They found that the activity and stability is positively correlated with the ionic liquid hydrophobicity, which was explained by the fact that the increase in hydrophobicity of the medium could allow the preservation of the essential water layer around the protein molecule, thus reducing direct protein-ion interactions.

On the contrary, the selectivity was found to be correlated positively with the hydrophobicity of the ionic liquid due to his higher capacity of reducing water activity (Aw) in the enzyme microenvironment [9]. Similar behavior was observed for other enzymes such as lipase from Pseudomonas sp. (PsL), CrL, Subtilisin and *Penicillin G acylase*

[2,15-17]. It has been observed that, with few exceptions, enzyme activity and solubility in ionic liquids are mutually exclusive.

Very recently the ionic liquid choline dihydrogen phosphate [Chol][H_2PO_4] was found to allowed over-laccase activity. The ionic liquid [Chol][H_2PO_4] was seen to be very effective at enhancing and stabilizing the laccase activity, due to the modications in the secondary structure of the enzymatic protein [12].

Green aspects of ionic liquids

Regarding to the consideration of ionic liquids as green solvents, different degrees of toxicity have been reported from ILs compared to that of chemicals currently used as solvent in chemical industry, which could be explained by the enormous variety of ionic liquids [18].

The most important property of ionic, in contrast to conventional solvents, is their negligible vapour pressure. That can result in lower emissions and consequently in a reduced exposure. Other advantage of the ionic liquids is the possibility of designing more environmentally friendly ionic liquids with improved biocatalytic behavior properties by changing or modifying either the anion or cation.

These process intensification methodologies could reduce and even eliminate the dependence on volatile organic solvents.

Isolation of reaction products from ionic liquids

In order to get an integral green process, it is necessary to corroborate that the reaction product is isolated from the ionic liquid medium without cross-contamination of the product with the ionic liquid. It could be reached by different ways considering the unique properties of ionic liquids: (i) distillation, (ii) extraction with water or organic solvents and (iii) extraction with supercritical carbon dioxide.

Distillation could be used when the reaction product are not labile since ionic liquid have low vapour pressure. Extraction with water or organic solvent could be used in the case that the ionic liquid was insoluble with the extraction solvent which can be reached by tailoring the hidrophobicity of the ionic liquid changing the anion or the cation composition [19].

However, the use of an organic solvent is not the best option if we pretend an integral ecofriendly system. In order to overcome the disadvantages of using organic solvents for the extraction of reaction products, it has been demonstrated that the extraction of organic compounds from ionic liquids by using supercritical carbon dioxide ($scCO_2$) is a promising option.

Meanwhile the $scCO_2$ can be solubilized in the ionic liquid phase, the ionic liquid shows very low solubility in the $scCO_2$ phase. As consequence the $scCO_2$ can extract organic substances from ionic liquids obtaining an extract free of contamination of ionic liquids provided that the ionic liquid is selected in an appropriate way [20,21].

Conclusion and Remarks

The number of publications related to the application of ionic liquids in biotechnology has increased exponentially during the last 15 years. The next step is the industrial application of the developments achieved. For that, it is essential to consider and address the following aspects: (i) scaling and development of continuous processes under real operating conditions, (ii) deeper study of toxicity and the impact of ionic liquids with the aim to design less toxic and biodegradable ILs which can be applied in industrial process (iii) the study of the cost-benefit and the economic and life-cycle analyses of processes.

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