

研究论文

离子液体的组成及溶剂性质与木瓜蛋白酶催化特性的关系

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收稿日期 2006-9-25 修回日期 网络版发布日期 2007-7-14 接受日期

摘要 离子液体的组成及溶剂性质对木瓜蛋白酶催化*D,L*-对羟基苯甘氨酸甲酯不对称水解反应有重要的影响。木瓜蛋白酶在含 $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$) 介质中表现出较高的活性、对映体选择性及稳定性, 而在含有 $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$, $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$ 的介质中表现较低的对映体值。在含有 $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$) 的介质中, 酶活性随离子液体的极性增大而提高, 但在含有 $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$, $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$ 的介质中随离子液体的极性增大反而降低。木瓜蛋白酶的对映体选择性和稳定性均随着离子液体的疏水性增大而提高。荧光分析结果表明, 离子液体对酶分子构象具有显著的影响。在 $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$) 的介质中, 木瓜蛋白酶的最大荧光发射波长(λ_{max})均蓝移, 而在含有 $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$ 或 $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$ 的介质中, λ_{max} 均红移。与 $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$) 相比, 在 $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$ 或 $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$ 中, 酶分子构象的变化较大, 暴露的疏水区域较多。

关键词 木瓜蛋白酶 离子液体 *D,L*-对羟基苯甘氨酸甲酯 催化特性 荧光光谱分析

分类号 [0625](#) [0641](#) [0643](#)

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Correlation Between Catalytic Characteristics of Papain and Components and Solvent Properties of Ionic Liquids

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Abstract The components and solvent properties of ionic liquids (ILs) show an important impact on papain-catalyzed asymmetric hydrolysis of *D,L*-*p*-hydroxyphenylglycine methyl ester (*D,L*-HPGME). The enzyme was more active, enantioselective and stable in the $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$)-based systems, while it was less active, enantioselective and stable in the systems involving $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$ or $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$. Papain's activity increased with increasing the polarity of the ILs $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$) and, conversely, decreased with increasing the polarity of the ILs $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$ or $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$. Also, the more hydrophobic the IL was, the more enantioselective and stable the papain was. Fluorescence spectroscopic analysis demonstrates that ILs had an obvious effect on papain's conformation. In the $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$)-containing systems, a blue-shift of the maximal emission (λ_{max}) of papain occurred, while a red-shift of λ_{max} took place in the systems involving $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$ or $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$. Papain's conformation changed greatly when the enzyme was placed in $C_4\text{MIm}\cdot\text{HSO}_4$, $C_4\text{MIm}\cdot\text{Cl}$, $C_4\text{MIm}\cdot\text{NO}_3$ or $C_4\text{MIm}\cdot\text{CH}_3\text{COO}$ -based systems compared to those with $C_n\text{MIm}\cdot\text{BF}_4$ ($n=2\sim6$), resulting in more exposure of hydrophobic regions of the enzyme.

Key words [Papain](#) [Ionic liquid](#) [D,L-p-Hydroxyphenylglycine methyl ester](#) [Catalytic characteristic](#) [Fluorescence spectroscopic analysis](#)

DOI:

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