超分子体系中的分子识别研究 5: 单-[6-(1-吡啶)-6-脱氧]-α-和γ-环糊精对氨基酸分子识别的热力学性质 刘育,张毅民,孙世新,张智慧,陈荣悌

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摘要 本文用分光光度滴定法测定了单-[6-(1-吡啶)-6-脱氧]-α-和γ-环糊精(1)和(3)

与一系列氨基酸在磷酸缓冲溶液中(pH=7.20), 25.0~40.0℃时形成超分子体系的稳定常数,

进而计算了配位焓和配位熵, 并与单-[6-(1-吡啶)-6-脱氧]-β-环糊精(2)的实验结果作了比较。化学计量法表明, 所有的氨基酸均与环糊精衍生物形成了1:1的超分子体系。从热力学的观点,

讨论了化学修饰环糊精和客体氨基酸的尺寸或形状适合、疏水效应、

范德华力和氢键等几种弱相互作用对形成超分子体系的贡献。研究结果发现,具有正电荷环糊精衍生物的吡啶基,作为一种分子探针不仅可以识别氨基酸生物分子的尺寸或形状之间的差异,而且还可以识别L/D-

型手性对映体之间的差异, 进一步表明了主-客体间的诱导楔合、

几何互补在分子受体选择性键合底物形成超分子体系中的重要作用。

关键词 分光光度法 <u>氨基酸</u> <u>吡啶 P</u> <u>热力学性质</u> <u>稳定常数</u> <u>环糊精</u> <u>化学修饰</u> <u>分子识别</u> 天津市自然科学基金 国家教委跨世纪人才基金 国家教委优秀教师基金

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Molecular recognition study on supramolecular system V. molecular recognition thermodynamics of amino acids by mono-[6-(1-pyridinio)-6-deoxy]- α - and γ -cyclodextrins

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Abstract The spectrophotometric titrations have been performed in buffered aqueous solution (pH=7.20) at $25\sim40\,^{\circ}\mathrm{C}$ to give the stability constants (logKs) and the thermodynamic parameters (\triangle H^O and \triangle SO) for the supramolecular system formed by various amino acids with mono-[6-(1-pyridinio)-6-deoxy]- α and γ -cyclodextrins (1) and (3), and the results were compared with the data reported for mono-[6-(1-pyridinio)-6-deoxy]- β -cyclodextrin (2). The supramolecular system stoichiometry is 1:1 for all amino acid inclusion complexation with host compounds (1) and (3). The contributions of the size-fit or shape-fit and the several weak forces working between chemically modified cyclodextrins and guest amino acids, which include van der Waals forces, hydrogen bonding, and hydrophobic interactions upon forming supramolecular system are discussed from a viewpoint of thermodynamics. The thermodynamic parameters obtained indicate that the cyclodextrin derivatives carrying one positively charged pyridinio moiety as a molecular probe can recognize not only the differences between the molecular size and shape of amino acids, but also the L/D-amino acid chiral isomer, it further indicates the important action of the molecular receptor upon the selectivity to combine substrate to form the supramolecular system.

Key words <u>SPECTROPHOTOMETRY</u> <u>AMINO ACID</u> <u>PYRIDINE P</u> <u>THERMODYNAMIC PROPERTIES</u> STABILITY CONSTANT CYCLODEXTRIN CHEMICLAL MODIFICATION OLECULAR RECOGNITION

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