

疏水-亲脂相互作用对反应活性的影响 **13: 羧甲基糖淀粉钠催化酯水解的溶剂效应**

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收稿日期 修回日期 网络版发布日期 接受日期

摘要 在H₂O, Me₂SO-H₂O, Dioxane-H₂O, t-BuOH-H₂O体系中, 羧甲基糖淀粉钠(NaCMA)对不同链长的羧酸对硝基苯酚酯的水解有显著的加速作用, 并表明, 即使在受物发生部分簇集的情况下, NaCMA的催化作用仍呈饱和和动力学。讨论了有机溶剂、受物的链长、

受物的聚集状态对包络络合物解离常数K_d及催化酯水解速率常数k_c的影响。实验结果表明, NaCMA-受物包络络合物在纯水中最稳定,

有机溶剂的存在不同程度地降低了NaCMA催化酯水解的能力和包络络合物的稳定性。

关键词 [钠化合物](#) [催化剂](#) [络合物](#) [水解](#) [活性](#) [羧酸酯](#) [溶剂效应](#) [反应速度常数](#) [离解平衡](#) [疏水性](#) [长链化合物](#) [硝基苯酚 P](#) [包合物](#) [糖淀粉](#) [羧甲基](#)

分类号 [0643](#) [0621.16](#)

The effect of hydrophobic-lipophilic interactions on chemical reactivity 13: Solvent effect on the sodium carboxymethylamylose-catalyzed hydrolysis of long chain esters

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Abstract The hydrolysis of p-nitrophenyl esters of carboxylic acids with various chain lengths, namely, octanoate, dodecanoate and hexadecanoate, are accelerated by sodium carboxymethylamylose (NaCMA) in Me₂SO-H₂O, dioxane-H₂O and tert-BuOH-H₂O. These NaCMA-catalyzed hydrolyses follow Michaelis-Menten saturation kinetics, even when the substrate concns. are already involved in aggregate formation, in other words, even when the substrate concns. are greater than the crit. aggregate concentration (CAgC). The dissociation constants (K_d) of the inclusion complexes of the substrates and NaCMA have been evaluated from the dependencies of the hydrolytic rate constants on the concentration of NaCMA. The fact that the smallest K_d value was found in pure water indicates that organic cosolvents always decrease the stabilities of these host-guest complexes. The order of the K_d scale, K_d(DMSO-H₂O) < K_d(dioxane-H₂O) < K_d(tert-BuOH-H₂O), agrees with the order of lipophilicities of the organic cosolvents represented by their Rekker's constants. The observed K_d values obtained with substrate concentration beyond the CAgC are larger than those obtained with substrate concns. lower than CAgC. This shows that the process of helical inclusion complex formation can compete with the process of aggregation.

Key words [SODIUM COMPOUNDS](#) [CATALYST](#) [COMPLEX COMPOUNDS](#) [HYDROLYSIS](#) [ACTIVITY](#) [CARBOXYLIC ACID ESTER](#) [SOLVENT EFFECT](#) [REACTION RATE CONSTANT](#) [DISSOCIATION](#) [EQUILIBRIUM](#) [HYDROPHOBIC PROPERTIES](#) [LONG CHAIN COMPOUND](#) [NITROPHENOL P](#) [CLATHRATES](#) [AMYLOSE](#) [CARBOXYMETHYL GROUP](#)

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