疏水-亲脂作用对反应性的影响III:

环糊精对碳氟表面活性剂的熵驱动包结以及亲脂作用对形成糖淀粉型包结物的贡献

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摘要 用表面张力-浓度曲线法系统地研究了环糊精(CD)和羧甲基糖淀粉钠(Na-CMA)与H(CF2)12CO2K(1),Cl (CF2)nCH2CH2N^+(CH3)3I^-[n=8(3),10(5)]和相应的碳氢表面活性剂(2,4和6)的相互作用.由于几何尺寸的限制, 碳氟表面活性剂不能与α-CD形成包结络合物,但3与β-CD形成的包结络合物的稳定性远大于相应的碳氢受物4、3与β-CD的相互作用是熵驱动过程,而C12H25N^+(CH3)3I^-(6)则是焓有利的.与具有"预组织化"内穴的CD不同, 糖淀粉的包结是与大分子从线团到螺旋构象变化的协同过程,由于缺乏宿主-受物间的亲脂相互作用,Na-CMA不能与所有的碳氟受物形成包结络合物.

关键词 表面活性剂 核磁共振谱法 环糊精 熵 离解平衡 疏水性质 表面张力 驱动 包合物 糖淀粉 全氟代烃

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The effect of hydrophobic-lipophilic interactions on chemical reactivity III: Contributions of hydrophobic interactions to the binding of fluorocarbon surfactants by \b\-cyclodextrin and of lipophilic interactions to the binding of hydrocarbon substrates

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Abstract With cyclodextrin (a- and b-CD) and Na carboxymethylamylose (Na-CMA) substrates, and with H(CF2) 12CO2K, CH3(CH2)10CO2K, Cl(CF2)8CH2CH2N+Me3I- (I), CH3(CH2)8CH2N+Me3I- (II), Cl(CF2) 10CH2CH2N+Me3I- and CH3(CH2)10CH2N+Me3I- (III) as guests, the different behaviors of fluorocarbon and hydrocarbon surfactants were studied by surface tension measurements. Limited cavity size prevents the inclusion of fluorocarbon surfactants by a-CD, but the binding by b-CD is stronger for the fluorocarbon (I) than that for its hydrocarbon analog (II). A comparison of the thermodn. parameters of the b-CD binding process for (I) and (III) reveals that for the former the binding process is driven by entropy or hydrophobic forces, but for the latter the process is enthalpy-favored. Notably, Na-CMA fails to bind the fluorocarbons. A crucial difference between the cyclodextrins and the amylose-type hosts lies in the fact that the former possess pre-organized cavities whereas the latter have to readjust their conformations from loose and extended helices with random coils to interrupted helices during the process of binding. Apparently, this extra energy requirement demands contributions from lipophilic interactions for accomplishment which do not exist between fluorocarbon chains and the hosts. Thus lipophilic forces are significant in hydrophobic-lipophilic interactions.

Key wordsSURFACTANTSNMR SPECTROMETRYCYCLODEXTRINENTROPYDISSOCIATIONEQUILIBRIUMHYDROPHOBIC PROPERTIESSURFACE TENSIONDRIVECLATHRATESAMYLOSEPERFLUORO-HYDROCARBON

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