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Poster 13

Investigation of Temperature Coefficients of Amide Protons of Helical Peptides in Aqueous TFE Solution

Jeong-Yong Suh and Byong-Seok Choi

Department of Chemistry, KAIST, Yusong-gu, Taejon, 305-701

Temperature coefficients of amide protons have been investigated by 2D NMR spectroscopy for helical peptides with a central proline (P14) and its alanine derivative (P14A) in an aqueous trifluoroethanol (TFE) solution. The profiles of chemical shifts, exchange rates and solvent perturbations of amide protons are compared with that of temperature coefficients. Temperature coefficients of each residue at three different TFE concentrations were also obtained. The periodicity of temperature coefficients coincided exactly with that of chemical shifts. Interestingly, the slowly exchanging amide protons in P14 showed the largest temperature dependence ($-\Delta\delta/\Delta T > 8$ ppb/K) and amide protons with weaker hydrogen bonds exhibited the smallest temperature dependence ($-\Delta\delta/\Delta T < 3$ ppb/K). Downfield shifted amide protons consistently showed smaller temperature dependence in their chemical shift. Peptides are normally in conformational equilibrium between the structured state and the coil state, and both of our peptides exhibited gradual loss of secondary structure upon temperature elevation (CD results). As the coil state increases in the population ensemble, the most affected hydrogen bonds would be those on the concave (hydrophobic) side of the helix. Moreover, the decrease of curvature in amphiphilic peptides during the thermal melting process may further contribute the periodicity of temperature coefficients. The unusual behavior of temperature dependence of amide protons in TFE solution may be partly explained by the variation of hydrogen bond lengths due to 1) the shift of conformational equilibrium and 2) the change of helical curvature.