00092

Poster 16

# NMR and Molecular modeling Studies on Charge Transfer Complexes of Bis-, Tris-viologen with Naphthalene Derivatives

Lee, Suk Kyoung, Lee, sanghyuk

Dept. of Chemistry, Ewha Womans Univ.

The charge-transfer(CT) complexation behavior between bis- or tris-viologen and electron donors with naphthalene group is studied by proton NMR spectroscopy and molecular modeling in aqueous media. The viologen groups in bisviologen are connected with an alkyl chain of various length (n=3, 4, 5, 6, 8). $\beta$-naphthol, 2-naphthalic acid (2-NA), 2,6-naphthalenedicarboxylic acid (2,6-NDA) are used as an electron donor.

Naphthol protons showed a large upfield shift upon adding bisviologens, which indicates formation of CT complexes where the viologen and the naphthyl groups have face-to-face geometry. Bisviologens showed much larger shifts than methyl viologen. This is attributed to the formation of sandwich type complexes, where bisviologen behaves as a molecular tweezer, whereas it is impossible for methyl viologen to form a sandwich type complex.

The formation constants of CT complexes are obtained by NMR titration method. The formation constants initially increases (up to n=5) as the chain length increases, and decreases as the chain becomes further longer. Enthalpy and entropy changes involved in CT complex formation were obtained from temperature dependence of the equilibrium constants. Enthalpy change for the sandwich type complex formation had a negative maximum value at n=5. This indicates that the tendency of the formation constants is dominated by the enthalpy factor.

Optimized structures of CT complexes were obtained from molecular mechanics and molecular dynamics simulation. The energy-minimized structures agree well with the observed chemical shift changes. The van der Waals interaction plays a significant role in CT complex formation of bisviologen with $\beta$-naphthol.

The CT complex formation constants of trisviologen were larger than those

of bisviologens. 2-NA (with 1 net charge) as electron donor had a smaller formation constant than 2,6-NDA. Therefore, electrostatic interaction plays an important role in the formation of CT complexes. Molecular modeling calculation shows that the open type complex is more stable than the sandwich type complex in trisviologen case. This can be interpreted as the favorable van der Waals interaction does not compensate the instabilization due to steric distortion to form the sandwich type complex.