

Characterization and differentiation of binding modes of water-soluble porphyrins at complexation with DNA

The influence of water soluble cationic meso-tetra-(4N-oxyethylpyridyl)porphyrin (H₂TOEPyP₄) and its metallocomplexes with Ni, Cu, Co, Zn on hydrodynamic and spectral behavior of DNA solutions has been studied by UV/Vis absorption and viscosity measurement. It was shown that the presence of planar porphyrins, such as H₂TOEPyP₄, NiTOEPyP₄ and CuTOEPyP₄ leads to an increase in viscosity at relatively small concentrations, and then decrease to stable values. Such behavior is explained by intercalation of these porphyrins in DNA structure, because the intercalation mode involves the insertion of a planar molecule between DNA base pairs, which results in a decrease in the DNA helical twist and lengthening of the DNA. Further decrease of viscosity is explained by saturation intercalation sites and occurs outside binding mode. But in the case of porphyrins with axial ligands, such as CoTOEPyP₄ and ZnTOEPyP₄, the hydrodynamic parameters decrease, which is explained by self-stacking of these porphyrins in DNA surface. This data are proved by spectral measurements. The results obtained from titration experiments were used for calculation of binding parameters: the binding constant K_b and the number of binding sites per base pair n . Obtained data reveal that K_b varies between $3.4 \times 10^6 \text{ M}^{-1}$ and $5.4 \times 10^6 \text{ M}^{-1}$ for a planar porphyrins, a range typical for intercalation mode interactions, and $5.6 \times 10^5 \text{ M}^{-1}$ and $1.8 \times 10^6 \text{ M}^{-1}$ for axially porphyrins. In addition the exclusion parameter n also testifies that at intercalation ($n \sim 2$) the adjacent base pairs are removed to place the planar molecules, and for outside binders to pack on the surface need too few places ($n \sim 0,5-1$). It is apparent that the binding is somewhat stronger at intercalation.

The viscometric and spectrophotometric measurements are in good agreement.