

Why is the compact state of DNA preferred at higher temperature?

Folding transition of a single DNA chain in the presence of a multivalent cation

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長鎖 DNA 分子は多価のカチオンを添加により、膨潤したコイルからコンパクトに折り畳まれた凝縮状態へと不連続な転移を起こす [1]。本研究では多価カチオン存在下において長鎖 DNA 分子の単分子観測を行い、温度依存性・塩濃度依存性について調べた。その結果、凝縮状態は高温側・低塩濃度側で凝縮状態が安定になった。コイル・凝縮状態は無秩序・秩序状態であるとそれぞれみなすことができるが、温度依存性の実験結果によると直感と反し高温側で秩序状態が安定になっており、この結果は凝縮に伴いエントロピーが増大することを示している。凝縮状態における系全体のエントロピーがコイル状態のそれよりも大きくする原因は、凝縮に伴いエントロピーが増大するようなイオン分布 (低分子、高分子イオンを含む分布) を形成するためであると考えられる。そこで、凝縮に伴い高低価数のイオン間に交換が生じるといったメカニズムを提案した。イオン交換とは、凝縮に伴い高価数のイオン (4 価カチオンとポリアニオン (DNA)) は凝縮していく一方、ポリアニオン (DNA) に凝縮していた低価数のイオン (1 価カチオンと 1 価アニオン) は押し出されバルク中に放出されるというものである。これら温度・塩濃度依存性の結果はこの凝縮に伴うイオン交換による系の並進エントロピー変化により説明できることを明らかにした [2]。

The environment presented by a solution can dramatically affect the morphology of polyelectrolyte molecules. For example, upon the addition of multivalent cations such as spermine(4+) or spermidine(3+), a giant DNA molecule undergoes a large discrete transition from an elongated coil into a folded compact state accompanied by a change in volume on the order of 10^{-4} -fold. About a decade ago, based on the direct observation of individual DNA molecules by fluorescent microscopy, it has been clarified that DNA compaction is largely discrete, i.e., a first-order phase transition [1].

To clarify the mechanism of DNA folding transition, I performed single-chain observation of long DNAs in the presence of a tetravalent cation (spermine), at various temperatures and monovalent salt concentrations. In figure 2, the compact state is preferred at higher temperatures, indicating that the system entropy increases with DNA compaction. The appearance of a folded compact state at a higher temperature is contrary to the expected result regarding temperature dependence, since it is generally understood that a coil state has greater entropy

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than the compact state due to elastic entropy. On the other, I examined the effect of a change in monovalent cation concentration. The compact state in the presence of tetravalent cation unfolded into the swollen coil state, by adding monovalent cation.

To explain the effects of temperature, I propose the ionic exchange between higher and lower valence ions of each sign in DNA compaction. The higher valence ions, tetravalent cations and polyvalent anion (DNA chain), are assembled or condensed into compact DNA. On the other hand, lower valence ions, monovalent cations and monovalent anions, are repelled into the bulk solution. Thus, the positive change in entropy originates from the change in translational entropy upon such ion exchange. Ionic exchange should be responsible for the temperature-dependence of DNA compaction. My model explains the effects of both temperature and the monovalent salt concentration in compaction [2].

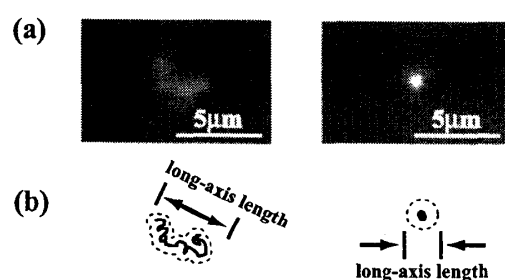


Figure 1: (a) Fluorescence images of single T4DNA molecules: (left) elongated coil state at 0.2 μM spermine; (right) folded compact state at 3.0 μM spermine. (b) Schematic representations of the fluorescence images and the actual conformations.

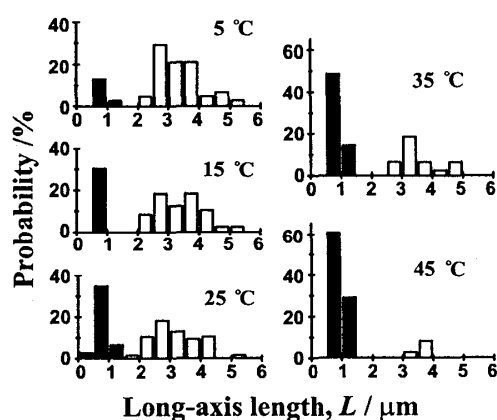


Figure 2: Histograms of the long-axis length, L , at different temperatures. The filled and open bars indicate the compact and coil states, respectively.

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References

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