



FIGURE 1 Birefringence Δ and optical density \blacktriangle as a function of temperature for yeast tRNA^{Phe}.

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METAL ION INTERACTIONS WITH FLUORESCENT DERIVATIVES OF NUCLEOTIDES

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The 1, *N*⁶-ethenoadenosine phosphate derivatives have been shown to be useful probes of nucleotide binding sites in a variety of enzymes (1). Perturbation of the etheno-

adenosine derivative with light results in formation of an excited-state compound that can undergo a variety of reactions within the time scale of its fluorescent lifetime, including deprotonation, rotational diffusion, and energy transfer to paramagnetic and colored metal cations near the chromophore. The rates of these reactions are a function of the excited-state lifetime and environmental factors such as the distance between the interacting molecules and the diffusional properties of the bound species. A comparison of the rates of the excited state decay when bound to the enzymatic site to those in solution reveals information of the binding site with respect to the spacial organization (distances between the metal and nucleotide) and the temporal organization (how fast the bound molecules diffuse).

In solution, high concentrations (>50 mM) of Ni(II), Co(II), and Mn(II) cations quench the fluorescence of ethenoadenosine derivatives by collisional quenching. At low concentrations (10^{-6} – 10^{-3} M) quenching occurs when the metal binds to the phosphates. The affinity constant depends upon the metal ion and the pH. The increase in the decay rate of the excited-state molecule by the bound metal is primarily a function of the spectral overlap in the metal absorption and the ethenoadenosine fluorescence emission. The effect on intersystem crossing rates by the unpaired electrons of the metal appears to be less significant.

The pK of ethenoadenosine in the excited state is lower than in the ground state. Excitation of the acid form results in emission from the base form, indicating that deprotonation occurs rapidly. Measuring fluorescence decay rates of the ethenoadenosine derivative as a function of pH allows one to calculate the rate of protonation and deprotonation of the excited-state species and then to compare with the quenching rates of the metal cations. The collisional rates for quenching are of the order $\text{Ni} \cong \text{Co} > \text{H}^+ > \text{Mn}$. It is interesting to note that the pH dependence of ethenoadenosine, etheno AMP, etheno ADP, and etheno ATP differ, indicating that the conformation of the molecule allows interaction between the adenosine ring and the phosphate.

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RUPTURE DIAPHRAGMLESS APPARATUS FOR PRESSURE-JUMP RELAXATION MEASUREMENT

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The kinetics of micelle formation and dissociation in solutions of anionic surfactants, such as sodium dodecyl and tetradecyl sulfates (SDS and STS), have been studied experimentally by various techniques. Recently a new theory of micelle formation mechanism was proposed together with experimental results obtained in the course of chemical relaxation studies of micellar solutions of ionic surfactants by Aniansson