STUDIES ON COPPER CHROMICYANIDE AS PREBIOTIC CATALYST

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Abstract. Interaction of ribonucleotides, namely 5′-AMP, 5′-GMP, 5′-CMP, and 5′-UMP with copper chromicyanide has been studied. Maximum adsorption was observed at neutral pH. The adsorption isotherms were found to be Langmuirian in nature. Copper chromicyanide was found to be effective adsorbent and purine nucleotides showed more adsorption than pyrimidine nucleotides. Infrared spectral studies suggested that the adsorption occurs due to interaction of phosphate moiety, N-1, N-3, and N-7 of ribonucleotide molecule and outer divalent copper ion present in the lattice of copper chromicyanide. Copper chromicyanide also has been found to be efficient in catalyzing the conversion of cysteine into cystine. The results of the present study support the hypothesis that the metal cyanogen complexes could have played important role in concentrating and stabilizing the biomonomers on their surfaces during the course of chemical evolution and could have acted as prebiotic catalyst.

1. Introduction

It is now widely accepted that a crucial step in chemical evolution on the earth involved the polymerization of important biomonomers such as amino acids, nucleotides, and pentose sugars which were formed from simple molecules under prebiotic environment, but till now it is not well established about how the biomonomers might have concentrated from their dilute aqueous solutions in primeval seas. However, one of the suggestions is that clays and other minerals have provided surfaces onto which small molecules could have been concentrated and might have undergone a class of reactions such as condensation, oligomerization, and redox reactions producing polymeric material from which life has emerged under prebiotic environment (Ferris and Kamaluddin, 1989; Ferris, 1999).

It is generally accepted that the transition metal ions abundantly present in primeval seas, might have complexed with simple molecules available to them. It has been reported that cyanide ions were readily formed under prebiotic environment. Since cyanide ion is strong field ligand, it is reasonable to assume that cyanide ions might have formed a number of insoluble and soluble cyano complexes with transition metal ions abundantly present in primeval seas. Arrhenious has proposed the existence of ferro-ferricyanide in Anoxic Archean Hydrosphere. Water insoluble metal cyanogen complexes might have locally settled at the bottom of sea or at sea shore. We propose that these metal cyanogen complexes might have concentrated the biomonomers on their surface through adsorption processes and subsequently catalyzed a class of reactions of prebiotic relevance.
Various metal ferrocyanides have been synthesized in our laboratory and their interaction with biomonomers such as amino acid, nitrogen bases and nucleotides have been studied suggesting their possible role in chemical evolution (Kamaluddin et al., 1990; Alam and Kamaluddin, 2000). They have been found to be efficient in catalyzing reactions of prebiotic relevance (Alam et al., 2000, 2002). We studied the interaction of 5’-ribonucleotides with copper chromicyanide to test its possible role in chemical evolution.

2. Experimental

Copper chromicyanide was synthesized from potassium chromicyanide by double decomposition method. Potassium chromicyanide was synthesized using Christensen’s method (Bigelow, 1946). 167 ml, 0.1M potassium chromicyanide solution was slowly added to 500 ml, 0.1M copper nitrate solution with constant stirring. After 24 h reaction mixture was filtered, washed with water, dried, ground and sieved to 80-mesh size. Characterization of the copper chromicyanide was done by CHN analysis, TGA, IR and X-ray diffraction studies.

The adsorption of all the four ribonucleotides on copper chromicyanide was studied at pH 4.0, 7.0 and 9.0 by adding 5 ml of 2.8\times10^{-4} M ribonucleotide solutions to 25 mg adsorbent each time. The suspensions were shaken initially for 1 h and then allowed to equilibrate at 30°C with intermittent shaking. After 24 h the suspensions were centrifuged at 8000 rpm and the supernatant liquid was decanted. The amount of adsorbed ribonucleotide was estimated from the difference between their concentrations before and after adsorption spectrophotometrically. The equilibrium concentration of ribonucleotide and the amount adsorbed were used to obtain adsorption isotherms.

3. Results and Discussion

For the chromicyanides of divalent metal ion, a general formula M_3[Cr(CN)_6]_2.nH_2O has been reported, where M^{2+} represents an exchangeable divalent transition metal ion. The [Cr(CN)_6]^{3-} ions possess an octahedral geometry in which Cr^{3+} is surrounded by six CN^- ligands and has electronic configuration of t^3_2g. One of the t^2g orbital has two electrons, second t^2g orbital has one unpaired electron whereas the third t^2g orbital remains empty because the electrons are filled against Hund’s rule in the presence of cyanide ligand which is strong field in nature. Although CN^- ligands bond with Cr through \sigma donation, Cr donates \pi electrons present in its d\pi orbital to antibonding p\pi orbital of CN^- producing sufficient back bonding character. The transition metal chromicyanides generally exist in a polymeric lattice structure with [Cr(CN)_6]^{3-} anions, in which another transition metal ions may be coordinated through the nitrogen end of the cyanide ligand.

3.1. INTERACTION OF RIBONUCLEOTIDES WITH COPPER CHROMICYANIDE

The preliminary adsorption studies were carried out over a wide pH range, and subsequent studies were performed at neutral pH, which exhibited the maximum adsorption. The adsorption data obtained at neutral pH and over a concentration range of adsorbate