## Session Lectures

### B1

### Reversed Micelles to Mimic Active Site of Metalloenzymes

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Reversed micelle is an aggregate of surfactant formed in an aprotic solvent that usually contains a small amount of water. The interior core of the reversed micelle, *i.e.* the micellar interface and the inner aqueous phase, provides a unique reaction field which mimics the structure and function of the enzyme active site. We would like to show that metal ions in reversed micelles behave in a way similar to those found in metalloenzymes.

The reversed micelle of CTACl in $CHCl_3$ solubilizes a considerable amount of halide or nitrate salts of cobalt(II), nickel(II) and copper(II) that are otherwise insoluble in simple apolar media. The cobalt and nickel ions undergo a structural transformation between tetrahedral and octahedral configurations in the cationic reversed micelle [1]. At low water concentrations in the micelle, the tetrahedral complex is favored. This is easily converted to the octahedral species by lowering the temperature (thermochromism) or simply by the addition of water (solvochromism). Cupric halides undergo a more complex structural transformation in cationic reversed micelles [2]. At low water concentrations a polymeric cupric complex bridged by halide ions is produced, which transforms into monomeric species with an increase in water concentration. The complex is converted eventually into an octahedral species at high water concentrations.

The halide bridge of the polymeric copper mentioned above is readily broken by either reduction to the cuprous ion with 2-mercaptoethanol or by the addition of such common ligands as imidazole and azide ion. In the latter case, the resulting imidazole-copper complex showed an electronic absorption spectrum with $\lambda_{max}$ at 810 nm. This spectrum resembles that of copper carbonic anhydrase, though the $\lambda_{max}$ is red shifted from the latter by ~80 nm.

The hydrolysis of norleucine p-nitrophenyl ester was accelerated drastically by copper ion in 0.10 *M* AOT reversed micelles in $CCl_4$ [3]. The effect of copper was maximal at low water concentration (~0.15 *M*) in the micelle, and a further increase in water concentration diminished the rate acceleration by the metal sharply. The intramolecular cyclization of the pyridoxal Schiff base of histidine is also affected by metal ions in reversed micelles [4]. Of interest is the fact that even the magnesium ion was effective in prohibiting cyclization in the micelle, while it is totally ineffective in non-micellar solutions. All these phenomena of metal ions may be explained by their 'naked' character in reversed micelles, especially at low water concentrations therein.

1 J. Sunamoto and T. Hamada, *Bull. Chem. Soc. Japan, 51,* 3130 (1978).
2 J. Sunamoto, H. Kondo, T. Hamada, S. Yamamoto, Y. Matsuda and Y. Murakami, *Inorg. Chem., 19,* 3668 (1980).
3 J. Sunamoto, H. Kondo and K. Akimaru, *Chem. Lett.*, 821 (1978).
4 J. Sunamoto, H. Kondo, J. Kikuchi, H. Yoshinaga and S. Takei, submitted to *J. Org. Chem.* for publication (1982).

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### B2

### The Role of Metals in the Initiation and the Development of Malignant Transformation

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The concentration of metal ions in DNA molecules of a malignant growth is higher than in the norm. The genetic consequences appearing in the DNA molecule as a result of mutations of certain type and of the penetration of metal ions into its structure are considered.

The present state of investigation of metal influence upon the structural and thermodynamic properties of DNA, histones and chromatin in the norm and in the malignant transformation is considered. Metals endogen-bound with DNA leave the latter susceptible to the influence of X-rays and certain antitumor preparations. The change in the physical properties (electronic density distribution, thermostability) of DNA, histones and their complexes in the case of cancer are interpreted from the view-point of the influence of endogen-bound metal ions on the

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