

## Bioinorganic and Bioorganic Chemistry

### Studies on the Formation of Complexes between Mn(II), Co(II), Ni(II) and Cu(II) Cations and Diphosphate, Adenosine Monophosphoric Acid and Adenosine Diphosphoric Acid Anions in Water-Tetramethyl Ammonium Bromide 0.2 M Medium

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The equilibria of the formation of complexes between the metallic cations  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  and the anionic ligands diphosphate ( $HP_2O_7^{3-}$ ,  $P_2O_7^{4-}$ ) adenosine monophosphoric ( $AMP^{2-}$ ) and adenosine diphosphoric ( $HADP^{2-}$ ,  $ADP^{3-}$ ) have been studied, in a water-TMA<sup>+</sup>Br<sup>-</sup> medium, by variable pH potentiometry and by pH-stat potentiometry [1, 2].

This work allows us essentially to admit the existence of four types of complexes [MHL, M(HL)<sub>2</sub>, ML, ML<sub>2</sub>] and to determine the values of their corresponding formation constants [1, 3-8]. The thermodynamic quantities corresponding to the formation of complexes have been determined by Van t'Hoff rule and by pH-stat calorimetry [9]. The values obtained by these two different methods are quite consistent and point out the importance of the variations of entropy ( $\Delta S$ ) in the formation of complexes (e.g. Table I).

With regard to the variations of entropy, the results show that the values of  $\Delta S$  are important and increasing with temperature. This phenomenon can be explained by a reorganization of the molecules of

the water of the medium between the metallic cations, the ligands and the resulting complexes, consequently to the important disappearance of electric charges.

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### The Formation and Structure of Cu(II)-Clupeine Z Complexes

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The interaction of metal ions with DNA and the role it plays in biological processes has been a field of

TABLE I. Comparison between the Results Obtained by Potentiometry and by Calorimetry, TMA<sup>+</sup>Br<sup>-</sup> 0.2 M Medium, pH = 7, at 25 °C.

Complexes	$\Delta H$ (Kcal/mol)		log K		$\Delta G$ (Kcal/mol)		$\Delta S$ (cal/mol)	
	pot.	cal.	pot.	cal.	pot.	cal.	pot.	cal.
CoAMP	-0.1	-0.18	2.34	2.37	-3.20	-3.22	10.40	10.18
NiAMP	-2.1	-2.46	2.46	2.48	-3.36	-3.38	3.5	3.05