

Summary

The thesis includes three chapters:

A general survey is given in chapter one about kinetics and mechanism of aquation of holageno pentaamminecobalt (III) complexes. Also, the biological importance and solvent effects on this reaction have been reviewed.

Chapter two discusses the practical part of this work. The preparation of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ has been discussed. Also, preliminary spectral measurements made on the complex at different media were analysed and discussed.

Chapter three represents the kinetic results of aquation of bromo pentaamminecobalt (III) ions at different temperatures in aqueous and in mixed aqueous organic solvent which are: water-DMF, water-NMA, water-EE and water-ME. The kinetic measurements were carried out in a wide range of the co-solvent, it was from 0.0 to 50% w/w of the organic solvent component. The rate of aquation was followed spectrophotometrically.

It was found that the isocomposition energy of activation increased with progressive addition of the organic solvent component. The thermodynamic properties of the activated complex ΔG^* , ΔH^* and ΔS^* were computed and analyzed. The non linear variations of ΔH^* and ΔS^* with the mole fraction of the organic solvent component showed a complicated pattern which was discussed in terms of change of water structure in presence of organic solvents. Moreover, the non linearity in ΔS^* variations is a criterion of specific solvation and indicates that the concept of random distribution of the two solvent components is not valid in the presence of strong hydrogen bonding. The isokinetic plots for the studied complex in different media were linear in all cases with isokinetic temperature values near to experimental temperatures indicating the existence of a compensation effect

which leads to small variations of ΔG^* on changing solvent composition. Variations of $\log k$ with $\log [H_2O]$ were linear. The slope of the relation was less than unity in most studied system. This indicates that the internal structure of the studied media suffered serious changes on addition of the organic solvent component. Plots of $\log k$ versus the inverse of relative permittivity (ϵ_r) were non linear in all studied mixed solvents indicating the differential effect of solvent on the initial and transition states. Also, this behavior was clearly evident from the variations of the relative free energy of transfer as a function of solvent mole fraction .

From all of the above the Id mechanism was suggested as a successful mechanism for the aquation reaction in the studied mixed solvents.