



Faculty of Science, Alexandria University

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Spectrophotometric Studies For The Solvolysis Of Cobalt(III) Complexes In Organic Aqueous Mixtures

A Thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Chemistry

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B.Sc. Special Degree in Chemistry,

Faculty of Science, Alexandria University, 2015.

2019

Summary

The thesis includes four chapters:

Chapter I includes an introduction on the important roles of transition metal complexes in the biological system, specially the Co(III) complexes which have great interest in biological area as well the industrial one.

Types of solvolysis reactions and mechanism of substitution of octahedral complexes specially for Co(III) complexes have been shown, also, the structure of water, classifications of solvents and thermodynamic properties of water-co-solvent mixtures.

It clarifies solvent structure and its differential effect on the initial or the transition state which affect the rate of solvolysis reaction.

Also, the correlations of the rate constants with the relative permittivities of the medium, Grunwald weistein Y-function and other empirical solvent scales. A considerable interest was given to the extra thermodynamic relationships and the free energy of transfer of single ions from water to water - organic co-solvent mixtures.

Chapter II includes the preparation of two complexes $\text{trans-[Co(3,4-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ and $\text{trans-[Co(3,5-dmpy)}_4\text{Cl}_2\text{]ClO}_4$. Also, it is devoted for the experimental part of the thesis that is concerned with the instrument used in physical measurements of this work which is T80+ UV-VIS spectrophotometer. It shows the spectra for the ultraviolet absorption for the two complexes $\text{trans-[Co(3,4-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ and $\text{trans-[Co(3,5-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ at different percentages of organic aqueous mixtures with time up till to the infinity time.

Chapter III includes the results for the solvolysis of $\text{trans-[Co(3,4-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ complex in water, water-1,4-dioxane, water-dimethyl sulphoxide and water-dimethyl formamide mixtures, as well $\text{trans-[Co(3,5-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ in water and water-dimethyl formamide mixture. The kinetic measurements were carried out in a wide range of co-solvents; it was from 0-60% (V/V)% for all the co-solvents. The reaction rate constant at constant solvent composition was measured in a range from 40 to 55°C.

Chapter IV discusses the experimental results in this work, the rate of reaction was found to vary as the co-solvent is progressively added to water and it was found generally, that the rate constants of solvolysis of $\text{trans-[Co(3,4-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ complex reveal a descending tendency in the order;

N,N-dimethylformamide > Water > 1,4-dioxane > Dimethyl Sulphoxide.

Also, $\text{trans-[Co(3,5-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ is faster than $\text{trans-[Co(3,4-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ in water-dimethyl formamide solvent mixtures.

Plots of $\log k$ against ϵ_r^{-1} or y -values are not linear; this may be attributed to a large differential effect of solvent structure on the initial and transition states.

While plots of ΔH^\ddagger and ΔS^\ddagger against the mole fraction of the co-solvents showed extrema and the errors of these plots which are not abnormal show that these extrema are real. As well, the plots of ΔG^\ddagger against the mole fraction of the co-solvents shows linearity, which attributed to the compensation effect between ΔH^\ddagger and ΔS^\ddagger .

The isokinetic plots of ΔH^\ddagger against ΔS^\ddagger of for $\text{trans-[Co(3,4-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ in water-DMF, water-DMSO and water-dioxane mixtures, as well as, $\text{trans-[Co(3,5-dmpy)}_4\text{Cl}_2\text{]ClO}_4$ in DMF-water mixture are all lie on the same straight line, indicating a close similarity in mechanism.

Also, the computed values of the isokinetic temperatures, T_{iso} , are within the experimental temperature values range, so that their reactions are called entropy controlled, which is an evidence for solute-solvent interaction plays an important role.

The free energy cycle was applied, showing that the difference of the free energies of transfer between the initial and the transition states were negative, for both complexes in all binary aqueous mixtures. This may be attributed to influence of solvent structure on the transition state is greater than initial state and the type of substituent groups as well as its position on pyridine ring have a very important effect on the solvation and the stability of the initial and transition state.