

## Summary of Thesis

### **INFLUENCE OF POLAR SOLVENTS UPON THE COMPLEX FORMATION BETWEEN CROWN ETHERS AND CATIONS IN NONPOLAR MEDIUM**

by

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The main goal of the present work concern the study of the complex formation between macrocyclic ligands such as crown ethers, cryptand [2.2.2], crown ether derivatives, and cyclodextrin with charged or uncharged substrates in different media. This study is important from the point of view of understanding the mechanism of biological transport, molecular recognition, and enzyme specific binding activities as well as extraction abilities of crown ethers. During the extraction process, water molecules are coextracted with the metal ions, metal complexes, and anions into the water-saturated organic solvent used. Up to date, there is little knowledge about the influence of the water molecule upon these processes.

First, the study of the complex formation between 18C6 and barium and ammonium perchlorate in mixtures of water-dioxan is performed by means of calorimetric titrations. The water-dioxan system allows a large range of dielectric permittivity. The stability constants and thermodynamic values for the formed complexes are determined.

Since chloroform is used as solvent in extraction experiments, the complex formation of alkali metal cations and ammonium as dibenzylthiocarbamate salts with crown ethers in chloroform is systematically investigated by means of calorimetric titrations. The most important problem in nonpolar solvent arises from the existence of ion pairs. In the case of ammonium salts, competitive measurements are carried out to underline the anion influence upon the complex formation. The influence of chloroform upon the complex formation between the crown ethers and cryptand [2.2.2], respectively, and the ammonium salts is observed by using in these experiments other halogenated solvents, e.g. dichloromethane, 1,2-dichloroethane.

Further, the interest is focused on the interactions between small quantities of polar solvent (like water) and crown ethers in chloroform. These interactions are studied by calorimetric measurements. For a better understanding of the influence of chloroform upon the complexation between crown ethers and water, chloroform is replaced by: dichloromethane, 1,2-dichloroethane, and carbon tetrachloride. Since the hydrogen bonds are responsible for the complex formation between crown ethers and water in the halogenated solvents, further investigations have been performed by replacing water by methanol, acetone and acetonitrile.

Once the impact of the polar solvents upon the solvation of the ligands in chloroform has been investigated, the focus of attention is laid on the reaction of crown ethers with cations in nonpolar medium with small amounts of polar solvents added. The aim is to get deeper insight into the solvation (hydration) of the salts. The experiments have been carried out by calorimetric titration. The interactions, the ligand nature, the concentrations of polar solvents, and the nature of nonpolar solvents involved in complexation have been analysed and discussed.

In order to double check the results, a new set of experiments has been performed by spectrophotometric measurements. The stability constants of the complex formation between the two ligands one aza-15-crown-5 derivative and one benzo-15-crown-5 derivative, and alkali ions as dibenzylthiocarbamate salts in chloroform are determined based on the spectral changes of the ligands in the presence of variable concentration of alkali metal cations in chloroform. The results are comparable with the ones obtained by calorimetric titrations.

Further, the complex formation of  $\alpha$ -cyclodextrin with uncharged guests, such as amides and nitriles, respectively, in aqueous solution has been investigated by calorimetric titration. The results demonstrate the influence of solvation changes during the complex formation of uncharged molecules with  $\alpha$ -cyclodextrin.