دانشگاه شهید بهشتی

دانشکده علوم

پایان نامه

بعنوان بخشی از فعالیتهای تحصیلی لازم برای اخذ درجه دکتری در

گرایش شیمی تجزیه

عنوان :

۱-کمپلکسهای انتقال بار برخی از آزاکراون اترها با الکترون پذیرنده های π و σ (بررسی سینتیکی و ترمودینامیکی)

۲ - ساخت الکترودهای یون گزین برای اندازه گیری یونهای I^- و Pb^{2+}.

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THESIS

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TITLE:

I:CHARGE TRANSFER COMPLEXES OF SOME AZA CROWN ETHERS WITH σ AND π ELECTRON ACCEPTORS (KINETIC AND THERMODYNAMIC INVESTIGATIONS).
II:PREPARATION OF ION SELECTIVE ELECTRODES FOR DETERMINATION OF I^- AND Pb^{2+} IONS.

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Dedicated to :

My parents

whom my life is indebted to them.

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ABSTRACT

Charge-Transfer Complexes of some

AzaCrown Ethers with σ and π

Electron Acceptors.

Kinetic and Thermodynamic Investigations

and

Preparation of

Ion Selective Electrodes for Determination

of I^- and Pb^{2+} Ions

by

Susan Sadeghi Bojd

In part one of the thesis, the charge-transfer complexes of some azacrown ethers with several σ and π acceptors were investigated in nonaqeous solutions in order to obtain some information about their stoichiometry, stability, kinetics and mechanism.

The complex formation between iodine, as σ acceptor, and 5,6,14,15 dibenzo 1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (DBDA15C4) have been studied spectrophotometrically in chloroform solution. The resulting charge-transfer complexes characterized by microchemical analysis, IR spectroscopy and Raman spectroscopy. The rate constant and stability constant for the formation of the complex were calculated.

The complex formation between DBDA15C4 and some polynitrophenol

derivatives such as 2,4,6-trinitrophenol, picric acid (TNP), as π acceptor have been studied spectophotometrically in chloroform solution. The resulting proton transfer-charge transfer complex characterized by microchemical analysis and IR spectroscopy. The equilibrium constants for the resulting complexes were evaluated from the non-linear least squares fitting of the absorbance mole ratio data. The enthalpies and entropies of the successive complexation reactions for DBDA15C4-TNP system were determined from the temperature dependences of the equilibrium constants. Similar investigation was done on diaza-18-crown 6.

The formation of molecular complexes with 1:1 stoichiometry between 2,4,6-trinitrophenol and aza-12-5 and aza-18-crown-6 in chloroform solutions were investigated spectrophotometrically. The resulting complexes were isolated and characterized by microchemical analysis, IR and NMR spectroscopy. The equilibrium constants of 1:1 adducts were evaluated from the non linear least square curve fitting of the absorbance-mole ratio data. The overall stability of 2,4,6-trinitrophenol complexe was found to vary in the order: aza 15-crown-5 > aza 18-crown-6 $\approx$ aza 12-crown-4. The kinetics of complex formation between 2,4,6-trinitrophenol and the aza-substituted crown ethers used were investigated and in all cases the results showed that occurence of an oscillating chemical reactions in solution. A proper model for the observed oscillation behaviour was proposed.

TNP, also was used for an extraction- spectrophotometric method for

the determination of trace amounts of ketoconazole as ion-pair complex. Ketoconazole is effectively extracted with TNP at pH 2.5 into chloroform, followed by spectrophotometric determination. Beer's law is obyed over the range 1-58 $\mu g.ml^{-1}$ and the Sandell's sensitivity for 0.001 absorbance unit is 57 $ng.cm^{-2}$. The procedure was applied to the determination of ketoconazole in its tablets and creams as well as its recovery from a blood serum sample.

In part two, preparation of two polyvinyl chloride membrane ion selective electrodes for I^- and pb^{2+} ions was reported. A Mn(II) salen complex was used for preparation of the iodide selective electrode. Tetraphenyl porphyrin (TPP) was used as the neutral carrier in ISE for pb^{2+} ions. Effects of the pH of test solution, the concentration of internal solution in the electrodes and the composition of the membranes were investigated. The former electrode gave linear response with Nernstian slope of 59 mV/decade in the concentration range of $4x10^{-5}$ - $1.0x10^{-1}$ M for iodide ions. The electrode based on TPP exhibits a Nernstian response for pb^{2+} ions over a concentration range of $2.4x10^{-5}$ - $1x10^{-2}$ M.

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