

سوف



7994V

بیتوتهی

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

σ و π (بررسی سینتیکی و ترمودینامیکی)

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

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شهریور ۱۳۷۷

۷۹۹۴۷

۱۳۸۶ / ۸ / ۲۷

کتابخانه مرکزی
تهران



SHAHID BEHESHTI UNIVERSITY

FACULTY OF SCIENCES-DEPARTMENT OF CHEMISTRY

THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDY IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY (PH. D)
IN ANALYTICAL CHEMISTRY

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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SEPTEMBER 1998

Dedicated to :

My parents

whom my life is indebted to them.

ACKNOWLEDGMENT:

I would like to acknowledge with great appreciation the excellent guidance supervision from Dr.Mojtaba Shamsipur during this study.

I would like to thank Dr.Ali Massoumi for his patience and encouragement during this work.

My thanks are also due to the members of evaluating committee,especially Mrs.Dr.A.Safavi, for their valuable suggestions.

I appreciated Dr.N.Alizadeh ,Dr.M.Gangalli Dr.A Moghimi and Dr.Fakhari for their sincere assistances.

A special word of appreciation must be expressed to the chairmans of faculty of sciences and department of chemistry in the Shahid Beheshti University,Dr.N.Safari and Dr.M.Zahedi.

I am extremely grateful of all my friends in the universities of Shahid Beheshti,Tehran and Razi whose cooperation led me to complete this work.

Special thanks are also offered to my parents and brother , Mohammad,for their encouragement during my education.

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

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In part one of the thesis, the charge-transfer complexes of some azacrown ethers with several σ and π acceptors were investigated in nonaqueous 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 spectrophotometrically 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 complexes 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 occurrence 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 obeyed over the range $1-58 \mu\text{g.ml}^{-1}$ 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 $4 \times 10^{-5} - 1.0 \times 10^{-1} \text{ M}$ for iodide ions. The electrode based on TPP exhibits a Nernstian response for pb^{2+} ions over a concentration range of $2.4 \times 10^{-5} - 1 \times 10^{-2} \text{ M}$.

Contents	Page
List of Tables	
List of Figures	

Part I

**Charge Transfer Complexes of
Some AzaCrown Ethers with σ
and π Electron Acceptors.**

Kinetic and Thermodynamic Investigations

Chapter I: Introduction

1.1.1 General Introduction	3
1.1.2 General Features of Charge-Transfer Complexes	5
1.1.2.1 Study of Charge-Transfer Complexes by Different Methods	9
1.1.2.2 Types of Charge-Transfer Complexes	11
1.1.2.2.1 Outer and Inner Complexes	12
1.1.2.2.2 Ion Pair Complexes	14
1.1.3 Oscillating Chemical Reactions	15

Chapter II: Literature Review

1.2.1 Study of Charge-Transfer Complexes of Iodine with Acyclic and Cyclic Amines	19
1.2.2 Study of Charge-Transfer Complexes of Picric Acid with Acyclic and Cyclic Amines	23
1.2.3 Study of Charge-Transfer complexes of DDQ, CHL and TCNQ with Acyclic and Cyclic Amine	28
1.2.4 Ketoconazole Determination Methods	31

**Chapter III: Spectroscopic Studies of the Complexation of Iodine with
5,6,14,15 Dibenzo-1,4-Dioxa-8,12 Diaza Cylopentadeca- 5,14-Dien**

1.3.3 Introduction	36
1.3.2 Experimental	37

1.3.2.1 Reagents.....	37
1.3.2.2 Apparatus	37
1.3.2.3 General procedure	38
1.3.3 Results and Discussion	39
Chapter IV: Spectroscopic Studies of the Complexation of Picric Acid with DBDA15C4, DA18C6, A18C6, A15C5 and A12C4 in Chlorform Solution: Thermodynamics, Kinetics and Mechanism	
1.4.1 Introduction	59
1.4.2 Experimental.....	60
1.4.3 Reagents	60
1.4.2.2 Apparatus	61
1.4.2.3 Results.....	61
1.4.2.3.1 Stoichiometry and Stability Constant of Monoaza Crown Ethers (A18C6, A15C5, A12C4) with Picric Acid.....	61
1.4.2.3.2 Stoichiometry, Stability Constants and Thermodynamic Parameters of Diazacrown Ethers (DBDA15C4, DA18C6) with Picric Acid.....	65
1.4.2.3.3 Kinetic Investigation	68
1.4.3 Discussion.....	70
1.4.3.1 Stoichiometry and Thermodynamics	70
1.4.3.2 Kinetic Investigation	77
Chapter V: Kinetic and Spectrophotometric Studies of Charge- Transfer Investigation of DBDA15C4 with CHL, DDQ and TCNQ	
1.5.1 Introduction	115
1.5.2 Experimental.....	116
1.5.2.1 Reagents	116
1.5.2.2 Apparatus	116
1.5.2.3 General procedure	116
1.5.3 Results and Discussion.....	118

1.5.3.1 Stoichiometry Investigation	118
1.5.3.1.1 CHL-DBDA15C4 system	118
1.5.3.1.2 DDQ-DBDA15C4 system.....	120
1.5.3.1.3 TCNQ-DBDA15C4 system	125
1.5.3.2 Kinetic Investigation.....	125
Chapter VI: An Extractive-Spectrophotometric Method for the Determination of Ketoconazole	
1.6.1 Introduction.....	144
1.6.2 Experimental.....	145
1.6.2.1 Reagents	145
1.6.2.2 Apparatus	146
1.6.2.3 General procedure	146
1.6.2.3.1 Tablet Sample Solution.....	147
1.6.2.3.2 Cream Sample Solution.....	147
1.6.2.3.3 Official potentiometric Method	147
1.6.3 Results and Discussion.....	148
1.6.3.1 Ketoconazole-Picric Acid Complexation.....	148
1.6.3.2 Ketoconazole Determination	148
1.6.3.3 Beer's Law Study.....	151
1.6.3.4 Interference study	151
1.6.3.5 Determination of Ketoconazole in Tablets and Creams	152
1.6.3.6 Recovery of Ketoconazole from Blood Serum.....	152

Part II

Preparation of Ion Selective

Electodes For Determination

I- and pb²⁺ Ions

Chapter I: Introduction

2.1.1 General Introduction.....	164
---------------------------------	-----

2.1.2 Constituents of Membrane Electrodes	166
2.1.3 Determination of Selectivity Coefficients.....	168

Chapter II: Literature Review

2.2.1 Anion Selective Electrodes, especially Iodide Ion Selective Electrode	174
2.2.2 Lead (II) Ion Selective Electrode	178

Chapter III: Iodide Selective Electrode

2.3.1 Introduction.....	182
2.3.2 Experimental.....	182
2.3.2.1 Reagents	182
2.3.2.2 Apparatus	183
2.3.2.3 General Procedure	183
2.3.3 Results and Discussion.....	184
2.3.3.1 Response Characteristic of the Electrode	184
2.3.3.2 Response Time.....	186
2.3.3.3 pH Effect.....	187
2.3.3.4 Selectivity of the Electrode	187
2.3.3.5 Application.....	187

Chapter IV: Lead (II) Selective Electrode

2.4.1 Introduction.....	199
2.4.2 Experimental.....	200
2.4.2.1 Reagents	200
2.4.2.2 Apparatus	200
2.4.2.3 General Procedure	201
2.4.3 Results and Discussion.....	201
2.4.3.1 Response Characteristic of the Electrode	201
2.4.3.2 Response Time.....	203
2.4.3.3 pH Effect.....	203
2.4.3.4 Selectivity of the Electrode	204

2.4.3.5 Application	205
References	217
Title page & Abstract in persian	

List of Tables

Table		Page
1.3.1	Absorbance - mole ratios of macrocycle : Iodine at wavelengths 508, 364 and 248 nm.....	46
1.3.2	Microchemical data, colour and melting points for two charge - transfer complex of DBDA15C4 with iodine	47
1.3.3	Infrared frequencies and tentative assignments for DBDA15C4 and its charge - transfer complex of $[(DBDA15C4)_2 I^+] \bar{I}_3$	47
1.3.4	Absorbance vs. DBDA15C4/ I_2 mole ratios data in chloroform solution at 508nm and various temperatures	48
1.3.5	Equilibrium constant for the formation of $[(DBDA15C4)_2 I^+] \bar{I}_3$ at various temperatures in $CHCl_3$ and CH_2Cl_2	49
1.3.6	Absorbance of the $[(DBDA15C4)_2 I^+] \bar{I}_3$ at different times ($\lambda = 364nm, [I_2] = 2.7 \times 10^{-4}M; \frac{Macrocycle}{Iodine} = 15$	50
1.3.7	Specific Conductance at different temperature.	50
1.4.1	Absorbance of anisol at different A18C6/TNP mole ratios in $CHCl_3$: $[anisol] = 3 \times 10^{-5}M$	83
1.4.2	Absorbance of T.N.T at different A18C6/TNP mole ratios in $CHCl_3$, $[T.N.T] = 5.0 \times 10^{-5}M$	83
1.4.3	Microchemical data, colour and melting points of the molecular complexes of TNP with aza crown ethers.....	84
1.4.4	Infrared frequencies and Tentative assignments for TNP, different aza crowns and their 1:1 complexes.	85
1.4.5	Microchemical data, colour and melting points for the two molecular adducts of diazacrown ethers, i.e., DBDA15C4 and DA18C6.	86
1.4.6	Infrared frequencies and tentative assignemnts for a) DA18C6 - b)DBDA15C4, TNP and their adducts.....	87

1.4.7	Equilibrium constants for the formation of 1:1 and 1:2 adducts between different azacrown ethers and nitrophenol derivatives at various temperature	89
1.4.8	H-NMR spectral data of A18C6,TNP and their 1:1 molecular complex	90
1.4.9	Calculated rate constant for the A18C6/TNP system based on the proposed kinetic model.	91
1.5.1	Microchemical data, colour and melting points for the molecular adducts of DDQ, CHL and TCNQ with DBDA15C4.....	129
1.5.2	Infrared frequencies and tentative assignments for DDQ, CHL and TCNQ/DBDA15C4 adducts.	130
1.5.3	Calculated rate constants for DBDA15C4-CHL, DBDA15C4-DDQ and DBDA15C4-TCNQ systems in chloroform and acetonitrile solution at various temperatures.	131
1.6.1	Effects of different organic solvents on the extraction efficiency of the ion - pair complex.....	154
1.6.2	Effect of number of extraction on the extraction efficiency of the ion - pair complex.	154
1.6.3	Analysis of ketoconazole in presence of imidazole by the proposed method.	155
1.6.4	Results of potentiometric titration of ketoconazole in a) tablet and b) cream in acetic acid glacial.....	155
1.6.5	Results of determination of ketoconazole in its Formulations.	156
2.3.1	Optimization of membrane ingredient for \bar{I} ion selective electrode.	188
2.3.2	Potential response of various anions at the presence of $10^{-3}M$ KI solution by the proposed electrode.	189
2.3.3	Effect of internal solution concentration on potentiometric response of \bar{I} ion - selective electrode.	190

2.3.4	Potential response of the \bar{I} anion selective electrode based on Mn(II) salen complex.	190
2.3.5	Response - time results of the \bar{I} ion - selective electrode.	191
2.3.6	pH effect on response of the proposed electrode.	191
2.3.7	Selectivity coefficients ($K_{I,x}^{pot}$) of various interfering ions. ...	192
2.3.8	Potentiometric titration results of 50.0ml of 10^{-3} KI solution with 0.1M $AgNO_3$ using the proposed sensor as an indicator electrode.	193
2.4.1	Optimization of membrane ingredients for Pb^{2+} ion selective electrode.	206
2.4.2	Potential response of various anions by the proposed electrode.	207
2.4.3	Effect of internal solution concentration on the potentiometric response of Pb^{2+} ion selective electrode.	208
2.4.4	Potential response results of the Pb^{2+} ion selective electrode based on TPP.	208
2.4.5	Response - time results of the Pb^{2+} ion-selective electrode.	209
2.4.6	pH effect on response of the proposed electrode.	209
2.4.7	Selectivity coefficients ($K_{Pb,M}^{pot}$) of various interfering ions.	210
2.4.8	Potentiometric titration results of 50.0 ml of 10^{-3} M $Pb(NO_3)_2$ ethanolic solution with 0.1M K_2CrO_4 using the proposed sensor as an indicator electrode.	211

List of Figures

Figure	Page
1.3.1 Absorption of 7.4×10^{-4} iodine in chloroform in the presence of concentrations of DBDA15C4.	52
1.3.2 Absorption spectra of iodine (A, 5×10^{-4} M), 1:1 Iodine - DBDA15C4(B, 5.0×10^{-4} M), 1:1 Iodine-tBAI (C 3.3×10^{-4} M), DBDA15C4 (D, 4.9×10^{-4} M) and TBAI (E, 4.6×10^{-4} M).	52
1.3.3 Plots of absorbance vs. DBDA15C4 / I ₂ mole ratio in chloroform at wavelength 248m.....	53
1.3.4 Absorption spectra of 2.7×10^{-4} M iodine in the presence of equimolar concentration of DBDA15C4.	53
1.3.5 Absorption spectra of the dissolved crystalline [(DBDA15C4) ₂ I] ⁺ I ₃ ⁻ and [(DBDA15C4) ₂ I] ⁺ I ⁻ complexes.	54
1.3.6 Resonance Raman spectrum of [(DBDA15C4) ₂ +I] ⁺ I ₃ ⁻	54
1.3.7 Plots of absorbance vs. DBDA15C4 : I ₂ mole ratio in chloroform solution at 508 nm and various temperatures.....	55
1.3.8 Computer fit of the plot of absorbance vs. DBDA15C4 : I ₂ mole ratio at 508 nm and 25°C.	56
1.3.9 Vant - Hoff plot for the evaluation of thermodynamic parameters of [(DBDA15C4) ₂ I] ⁺ I ₃ ⁻ complex.	57
1.3.10 The relation between specific conductivity and temperature... ..	58
1.3.11 Vant - Hoff plot for the evaluation of activation energy of [(DBDA15C4) ₂ I] ⁺ I ₃ ⁻	58
1.4.1 Electronic absorption spectra of 5.0×10^{-5} M TNP in the presence of increasing concentration of A18C6.....	92
1.4.2 Plot of absorbance vs. A18C6/TNP mole ratio in CHCl ₃ of 410nm.....	93
1.4.3 Continuous variation plot at A18C6/TNP system.	93
1.4.4 A) Electronic absorption spectra of 3×10^{-5} M TNP in	

	the presence of increasing concentration of A15C5 (B) corresponding mole ratio and continuous variation plots.	94
1.4.5	Titration of $5 \times 10^{-5} \text{M}$ solution of A18C6 with TNP in CHCl_3 at varying mole ratios of TNP/A18C6.....	95
1.4.6	Titration of $3 \times 10^{-5} \text{M}$ solution of 3,5 dinitrobenzoic acid with A18C6 in CHCl_3	96
1.4.7	Proton NMR spectra of TNP at various A18C6/TNP mole ratios in CHCl_3	97
1.4.8	Absorbance - mole plots for A18C6-DNP (A) and A18C6-TNP (B) and chemical shift - mole ratio plot for A18C6-TNP (C) system in chloroform solution.	98
1.4.9	Absorption spectra of different nitrophenol derivatives in CHCl_3 in the presence of various concentration of DBDA15C4.....	99
1.4.10	Absorbance - mole ratio plots of DBDA15C4/nitrophenol at $\lambda=410\text{nm}$ in CHCl_3 solution.	100
1.4.11	Titration of $3.2 \times 10^{-5} \text{M}$ solution of 3,5 dinitrobenzoic acid with DBDA15C4 at different DBDA15C4/Acid mole ratios.	101
1.4.12	Continuous variation plots for DBDA15C4/TNP system in CHCl_3 . 102	
1.4.13	Plots of absorbance vs. $[\text{DBDA15C4}]/[\text{TNP}]$ mole ratios at various temperatures in CHCl_3	103
1.4.14	Competitive titration of DBDA15C4/TNP system with DDQ. 104	
1.4.15	Electronic absorption of DNP and TNP in the presence of increasing concentration of DA18C6.	105
1.4.16	Absorbance - mole ratios plot of DA18C6/TNP in CHCl_3	106
1.4.17	Absorbance - time plots at 410nm for a) DBDA15C4-TNP b) A18C6-TNP and c) DA18C6/A18C6/18C6-TNP systems at different mole ratios of azacrown ethers / TNP in chloroform solution at 25°C	107
1.4.18	structure of DBDA15C4 and its 1:2 complex with	

TNP.....	109
1.4.19 Computer fit of the plot of absorbance vs. [DBDA15C4]/[TNP] mole ratios obtained at 410nm.....	110
1.4.20 Computer fit of the plots of absorbance vs. [A18C6]/[TNP] and [A18C6]/[DNP] mole ratios.	111
1.4.21 Van't - Hoff plot for evaluation of thermodynamic parameters of DBDA15C4-TNP system.	112
1.4.22 Computer fit of the absorbance - time plot of A18C6-TNP system [TNP] = 2.510×10^{-5} and $\frac{[A18C6]}{[TNP]} = 0.028$ (A) and 0.050 (B).....	113
1.5.1 UV - Vis spectra of a mixture of CHL and DBDA15C4 in chloroform solution at different times.	132
1.5.2 UV - Vis spectra of DDQ and DBDA15C4 in chloroform solution at different times.	133
1.5.3 UV - Vis spectra of a mixture of TCNQ and DBDA15C4 in chloroform solution at different times.	134
1.5.4 A) Conductivity vs.mole fraction and B) Absorbance vs. mole ratio of CHL plot for the DBDA15C4-CHL system in acetonitrile	135
1.5.5 DA - mole ratios plot for a mixture of DDQ (3.0×10^{-4} M) and DBDA15C4 (0.02M) in chloroform solution.	136
1.6.1 Absorption spectra of 2.5×10^{-5} M of (a) ketoconazole and (b) picric acid in the presence of-increasing concentration of picric acid in the presence of increasing concentration of picnic acid and ketoconazole respectively in chloroform at 25°C	157
1.6.2 A) Absorbance - mole ratio and B) continous variations plots for ketoconazole - picric acid in chloroform at 25°C.....	158
1.6.3 computer fit of the plot of absorbance vs. [Ketoconazole] / [TNP] mole ratios.	158
1.6.4 Effect of pH on the extraction of ketoconazole.	159

1.6.5	Effects of volume of citrate buffer at (a) pH 2.5 and (b) volume of 0.1% w/v picric acid on the extraction of $6.9 \mu\text{g.ml}^{-1}$ ketoconazole.	159
1.6.6	Calibration graph for the determination of ketoconazole under the optimum conditions.	160
1.6.7	Potentiometric titration of a ketoconazole tablet sample dissolved in 30ml glacial acetic acid with 0.105M perchloric acid.	161
1.6.8	Potentiometric titration of a ketoconazole cream sample dissolved in 30ml glacial acetic acid with 0.105M perchloric acid.	161
2.3.1	Potential response of various anions at the presence of iodide anion based on the proposed electrode.	194
2.3.2	Effect of internal solution on response of electrode.	195
2.3.3	Potential response of the $\bar{\text{I}}$ electrode based on Mn(II) salen complex.	195
2.3.4	Response - time profile of the $\bar{\text{I}}$ ions selective electrode based on Mn(II) salen complex.	196
2.3.5	Response - pH profile of $\bar{\text{I}}$ ion - selective electrode based on the proposed electrode.	196
2.3.6	Potentiometric titration curve of 50.0ml of $1 \times 10^{-3}\text{M}$ KI solution with 0.1M AgNO_3 using the proposed sensor as an indicator electrode.	197
2.4.1	Potential response of various metal - ion selective electrodes based on TPP.	212
2.4.2	Effect of internal solution on response of electrode.	213
2.4.3	Potential - response of pb^{2+} - ion selective electrode based on TPP.	214
2.4.4	Response - time profile of pb^{2+} ion selective electrode.	215
2.4.5	Response - pH profile of pb^{2+} ion selective electrode based on TPP.	215