A Cyclic Voltammetry Study of Complexes between Viologens and Some Macrocyclic Molecules

By
Banan Malik Bani Ata

Supervisor
Dr. Shehadeh Mizyed

Co-Advisor
Dr. AbdelMonem Rawashdeh

Main Subject: Physical Organic Chemistry

June 2010
A Cyclic Voltammetry Study of complexes between Viologens and Some Macrocyclic Molecules

By
Banan Malik Bani Ata

Supervisor
Dr. Shehadeh Mizyed

Co-Advisor
Dr. AbdelMonem Rawashdeh

Subject
Physical Organic Chemistry

June 2010
Dedication

To my

Lovely Father

Lovely Mother

Lovely Betrothed

**Jamil**

Lovely Sisters

Lovely Brothers

And before of all to spirit of my grandparents

Banan Malik Bani Ata
Acknowledgment

First, praise and thanks for “Almighty Allah” from whom I always receive assistance and protection. I would like to express my greatest gratitude to my grandparents (Abu-Marouf and Um-Marouf) for their continuous pray.

I would like to express my sense of gratitude and my deepest thanks to my loving father and loving mother for their encouragement me and for their continuous support and understanding without whom the finalization of this work would not have been done.

I would like to express my greatest gratitude and very special thanks to my loving betrothed (Jamil) for his encouragement, support and understanding and for his patience from which I received my success, I was able to overcome all difficulties that I had and forgot all the hardships.

I would like to express my greatest gratitude to my sisters (Bshaer, Shifa', Lama and Batool), my brothers (Bashar and Eba'a), my uncles (Dr.Jamil, Dr.Marouf, Ezeddin, Borhan, Seif and Noor), my Father and Mother-in-law (Abu-Malik and Um Malik) and to all my relatives for their encouragement.
Then, I would like to express my deepest thanks to Dr. Shehadeh Mizyed and Dr. Abdel-Monem Rawashdeh for their direct supervision, help and encouragement throughout the course of this work.

I would like to thank the committee members; prof. Dr. Deeb Marji, prof. Dr. Sabri Mahmmod and prof. Dr. Khamis Abbas.

I would like to thank the teaching staff of the Chemistry Department at Yarmouk University.

I would like to thank all the employees in the Chemistry Department especially Fadwa Bani-Hani.

I would like to express special thanks to Dr. Abd-Allah Jrrah, Dr. Rshid Jrrah and Dr. Hussein E'ebedat.

Finally, I would like to thank all my friends.
A Cyclic Voltammetry Study of complexes between Viologens and Some Macro cyclic Molecules

By

Banan Malik Bani Ata

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science at the Chemistry Department, Yarmouk University, Irbid, Jordan, 2010.

June 2010

Committee members:

Dr. Shehadeh Mizyed
Associate Prof. Organic Chemistry

Dr. AbdelMonem Rawashdeh
Associate Prof. Organic Chemistry

Prof. Dr. Sabri Mahmmood
Professor, Inorganic Chemistry

Prof. Dr. Khamis Abbas
Professor, Organic Chemistry

Prof. Dr. Deeb Marji
Professor, Physical Chemistry
(Al al-Bayt University)
## Tables of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>V</td>
</tr>
<tr>
<td>List of Figures</td>
<td>VIII</td>
</tr>
<tr>
<td>Abstract</td>
<td>XVIII</td>
</tr>
<tr>
<td>Chapter One</td>
<td></td>
</tr>
<tr>
<td>1.A: Introduction</td>
<td>2</td>
</tr>
<tr>
<td>1.A.1: Viologens</td>
<td>2</td>
</tr>
<tr>
<td>1.A.2: Crown ethers</td>
<td>5</td>
</tr>
<tr>
<td>1.A.3: Schiff Bases Crown Ethers</td>
<td>8</td>
</tr>
<tr>
<td>1.B: Complexation Study</td>
<td>9</td>
</tr>
<tr>
<td>1.B.1: Supramolecular Chemistry</td>
<td>9</td>
</tr>
<tr>
<td>1.B.2: Host-Guest Chemistry</td>
<td>10</td>
</tr>
<tr>
<td>1.B.2.1: Electrostatic interactions</td>
<td>11</td>
</tr>
<tr>
<td>1.B.2.1.a: Ion-Ion interactions</td>
<td>11</td>
</tr>
<tr>
<td>1.B.2.1.b: Ion-Dipole interactions</td>
<td>11</td>
</tr>
<tr>
<td>1.B.2.1.c: Dipole-Dipole interactions</td>
<td>12</td>
</tr>
<tr>
<td>1.B.2.2: π-π interactions (π-stacking interactions)</td>
<td>12</td>
</tr>
<tr>
<td>1.B.2.3: π-cation interactions</td>
<td>12</td>
</tr>
<tr>
<td>1.B.3: Charge transfer complexes</td>
<td>13</td>
</tr>
<tr>
<td>I. Complexes of macromolecules with viologens</td>
<td>14</td>
</tr>
<tr>
<td>II. Complexes of Crown Ethers with C₆₀</td>
<td>17</td>
</tr>
<tr>
<td>III. Complexes of schiff-base with C₆₀</td>
<td>18</td>
</tr>
</tbody>
</table>
1.C: Electroanalytical Chemistry
   1.C.1: Electrochemical cell
   1.C.2: Electroanalytical methods

1.C.2.1: Voltammetry
   1.C.2.1.a: Electrodes
   1.C.2.1.b: Types of voltammetry
      I. Linear sweep voltammetry
      II. Staircase voltammetry
      III. Squarewave voltammetry
      IV. Cyclic voltammetry
         IV.a. Reversible electrode reactions
         IV.b. Applications of cyclic voltammetry

1. D: Aims of the Present Work

**Chapter Two**

<table>
<thead>
<tr>
<th>2.A:</th>
<th>Experimental</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.A.1:</td>
<td>Chemicals</td>
<td>38</td>
</tr>
<tr>
<td>2.A.1.1:</td>
<td>Preparation of methyl viologen diperchlorate from methyl viologen dichloride</td>
<td>39</td>
</tr>
<tr>
<td>2.A.1.2:</td>
<td>Preparation of tetrabutylammonium perchlorate (TBAP)</td>
<td>39</td>
</tr>
<tr>
<td>2.A.1.3:</td>
<td>Preparation of schiff base crown ether</td>
<td>40</td>
</tr>
<tr>
<td>2.A.2:</td>
<td>Instrumentation and Material</td>
<td>42</td>
</tr>
</tbody>
</table>
Chapter Three

3.A: Results

3.A.1: Cyclic voltammetry of methyl viologen (MV) 47
3.A.2: Complexation of crown ethers with viologens 50

3.A.2.1: Complexation of benzo-18-crown-6 with MV 52
3.A.2.2: Complexation of benzo-18-crown-6 with BV 54
3.A.2.3: Complexation of benzo-15-crown-5 with MV 57
3.A.2.4: Complexation of benzo-15-crown-5 with BV 59
3.A.2.5: Complexation of 18-crown-6 with MV 62
3.A.2.6: Complexation of 18-crown-6 with BV 64
3.A.2.7: Complexation of N-phenylaza-15-crown-5 with MV 67
3.A.2.8: Complexation of N-phenylaza-15-crown-5 with BV 69
3.A.2.9: Complexation of dicyclohexyl-18-crown-6 with MV 72
3.A.2.10: Complexation of dicyclohexyl-18-crown-6 with BV 74
3.A.2.11: Complexation of 1,10-diaza-18-crown-6 with MV 77
3.A.2.12: Complexation of 1,10-diaza-18-crown-6 with BV 79
3.A.2.14: Complexation of dibenzodiaza-15-crown-4 with BV 84
3.A.2.15: Complexation of [2,2,2]cryptand with MV 87
3.A.2.16: Complexation of [2,2,2]cryptand with BV 89
3.A.2.17: Complexation of schiff base crown ether with MV 92
3.A.2.18: Complexation of Schiff base crown ether with BV 94

3.B: Discussion 100

3.B.1: The complexes of MV with oxygen containing hosts 100
3.B.2: The complexes of MV with nitrogen containing hosts 102
3.B.3: The complexes of BV with oxygen containing hosts 106
3.B.4: The complexes of BV with nitrogen containing hosts 107

3.C: Conclusion 111

References 113
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table (2-1):</td>
<td>A list of chemical reagents used, their grades and suppliers</td>
<td>38</td>
</tr>
<tr>
<td>Table (3-1):</td>
<td>The values of scan rates and cathodic peaks current obtained from CV curves of MV</td>
<td>49</td>
</tr>
<tr>
<td>Table (3-2):</td>
<td>The peak to peak separation ($\Delta E$) and half-wave potential ($E_{w}$) for each case for the first and second electrons transfer for benzo-18-crown-6 (8) with MV</td>
<td>53</td>
</tr>
<tr>
<td>Table (3-3):</td>
<td>The peak to peak separation ($\Delta E$) and half-wave potential ($E_{w}$) for each case for the first and second electrons transfer for benzo-18-crown-6 (8) with BV</td>
<td>55</td>
</tr>
<tr>
<td>Table (3-4):</td>
<td>The peak to peak separation ($\Delta E$) and half-wave potential ($E_{w}$) for each case for the first and second electrons transfer for benzo-15-crown-5 (9) with MV</td>
<td>58</td>
</tr>
<tr>
<td>Table (3-5):</td>
<td>The peak to peak separation ($\Delta E$) and half-wave potential ($E_{w}$) for each case for the first and second electrons transfer for benzo-15-crown-5 (9) with BV</td>
<td>60</td>
</tr>
<tr>
<td>Table (3-6):</td>
<td>The peak to peak separation ($\Delta E$) and half-wave potential ($E_{w}$) for each case for the first and second electrons transfer for 18-crown-6 (7) with MV</td>
<td>63</td>
</tr>
<tr>
<td>Table (3-7):</td>
<td>The peak to peak separation ($\Delta E$) and half-wave potential ($E_{w}$) for each case for the first and second electrons transfer for 18-crown-6 (7) with BV</td>
<td>65</td>
</tr>
</tbody>
</table>
Table (3-8): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for N-phenylaza-15-crown-5 (29) with MV

Table (3-9): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for N-phenylaza-15-crown-5 (29) with BV

Table (3-10): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for dicyclohexyl-18-crown-6 (30) with MV

Table (3-11): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for dicyclohexyl-18-crown-6 (30) with BV

Table (3-12): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for 1,10-diaza-18-crown-6 (11) with MV

Table (3-13): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for 1,10-diaza-18-crown-6 (11) with BV

Table (3-14): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for dibenzodiaza-15-crown-4 (19) with MV

Table (3-15): The peak to peak separation ($\Delta E$) and half-wave potential ($E_{1/2}$) for each case for the first and second electrons transfer for dibenzodiaza-15-crown-4 (19) with BV