

ARTICLE

**Complexation Between Viologens and Some Macrocyclic Molecules:
A Cyclic Voltammetry Study****Abdel Monem Rawashdeh^{*}, Banan Malik Bani Ata, Deeb Marji and
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Abstract: Intermolecular interactions between methyl viologen (MV) and benzyl viologen (BV) with macrocyclic molecules (1), (2), (3), (4), (5), (6), (7), (8) and Schiff base crown ether (9) are investigated in acetonitrile solution and in the presence of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. The formation constants of the charge transfer (CT) complexes between viologens and macromolecules were determined for the first and the second reduction process at room temperature using cyclic voltammetry at 100 mV/s as a scan rate. The redox potential of all complexes (E) was determined and peak to peak separation (PP) and half-wave potential ($E_{1/2}$) were measured for these complexes. Complexes were found to have 1:1 macrocyclic molecules to viologens stoichiometry.

Keywords: Cyclic voltammetry, Macrocyclic molecules, Crown ethers, Viologens.

Introduction

Viologens are diquatery derivatives of 4,4'-bipyridyl^[1]. These compounds are well known as electrochromic compounds that have a dicationic form, and have their names from the color change from colorless to violet upon oxidation to radical cation form under exposure to a photo source^[2,3].

Viologens (V) are considered electron-deficient species that are capable of forming charge transfer complexes with some electron donating molecules^[4,5]. Those compounds are easily reduced to an intensely blue colored radical mono-cation form which is easily returned to the dication form in the presence of oxygen.

There are three common redox states of viologens: a dication (V^{2+}) which represents the

most stable form, a radical cation ($V^{\cdot+}$) and di-reduced neutral compound (V)^[6,7].

Crown ethers are neutral macrocyclic polyethers that contain several oxygen atoms separated by (CH_2CH_2) groups^[8]. They have a specific shape in which oxygen atoms are oriented into a ring as a hydrophilic part, while (CH_2-CH_2) groups are oriented outside the ring as a lipophilic part^[8]. Cryptands are bicyclic hosts with two points connected by at least three bridges, which were firstly prepared in 1968^[9].

In crown ethers and cryptands, each oxygen atom carries a partially negative charge, which makes them suitable to form complexes with positively charged metal ions or with partially positively charged molecules *via* electrostatic attraction^[9].

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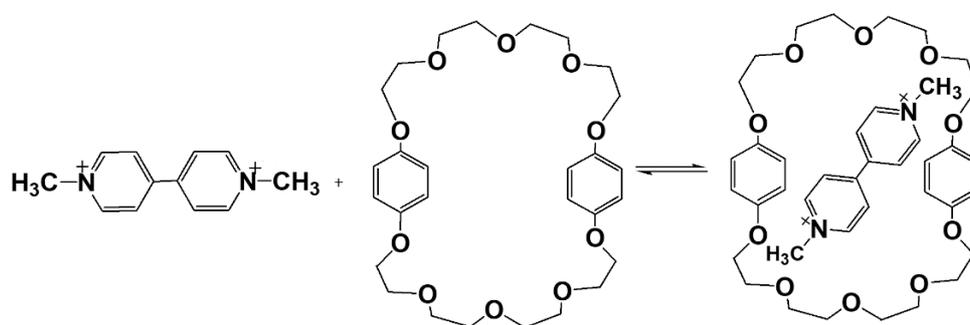
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Schiff Base Crown Ethers are macrocyclic crown ethers with a carbon-nitrogen double bond. They behave as electron donors; therefore, they have been widely studied as complexing agents with transition metals, alkali and alkaline earth metals^[10-12].

Charge transfer complexes are generally formed between electron-rich hosts, such as crown ethers, cryptands, Schiff Base Crown Ethers or other macrocyclic compounds with electron-poor guests, such as viologens, in particular methyl and benzyl viologens. Yasuda *et al.*^[13] studied the charge transfer complexes between benzyl viologen (BV), 4,4-

dicyanophenylbipyridinium (CyV) with α , β and γ -cyclodextrin (CD), using cyclic voltammetry and spectroelectrochemical methods. They have found that the reduced state of BV, forms inclusion complexes with α -CD and γ -CD, while both oxidized and reduced states of BV form inclusion complexes with β -CD. Kim *et al.*^[14] studied the inclusion behavior of dicationic methyl viologen and its reduced species with cucurbit[7]uril (CB[7]), using various spectroscopic and electrochemical methods. They have found that CB[7] forms a very stable 1:1 inclusion complex with MV^{2+} .

Scheme 1. Schematic representation of complexation of methylviologen and *p*-benzocrown ether^[15].



Ashton *et al.*^[15] reported the formation of 1:1 inclusion complex between methyl viologen and *p*-benzocrown ether in solution. They noted that the binding constants are similar to those of benzyl viologen at 25°C in water.

Our group has studied the charge transfer complex formation between methyl, benzyl and ethyl viologens with Dibenzo-diaza-15-crown-4 and several other complexes in ethanol solution. The formation constants of the complexes were determined at different temperatures using UV-Vis spectroscopy. The charge transfer complexes were found to have either 1:1 or 2:1 crown ether: viologen complexes^[16].

Cyclic voltammetry is widely used to study charge transfer complex formation. It proved to be an effective, precise and sensitive method for such studies. Tomokazu *et al.*^[17] studied the complexation of methyl viologens with cyclodextrins at 25°C in phosphate buffer (PH=7) using glassy carbon disk as a working electrode. They found that β -CD binds the species in the order of $MV > MV^+ > MV^{2+}$. When the host-guest complexation between MV^{2+} and cucurbit[8]uril (CB[8]) was investigated^[18], two extra redox waves were

detected, beside that of the free MV, indicating the formation of 1:1 inclusion complex.

The present study is intended to investigate the complexation of (1), (2), (3), (4), (5), (6), (7), (8) and a Schiff base crown ether (9) with methyl (MV) and benzyl viologens (BV) in acetonitrile and in the presence of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, by using cyclic voltammetry, as well as to measure redox potentials of the complexes, determine the half-wave potential ($E_{1/2}$) and calculate the formation constant for each case.

Experimental Chemicals

The chemical reagents, grades and their suppliers' names used in this study are shown here: 18-Crown-6 ($\geq 99\%$), Dibenzodiaz-15-Crown-4 ($> 98\%$), 1,10-Diaza-18-Crown-6 ($>97\%$), [2,2,2]Cryptand ($\geq 99\%$) and tetrabutylammonium bromide ($> 97\%$) were purchased from FLUKA. Dicyclohexyl-18-Crown-6 ($>98\%$), Benzo-18-Crown-6 ($>99\%$), 4,5-Dimethylphenylendiamine ($> 98\%$) and 1,2-Dibromethane (99%) were purchased from

MERCK. Benzo-15-Crown-4 (99%), Phenylaza-15-Crown-5 (98%) and 2-Hydroxynaphthaldehyde were purchased from ACROS. Benzyl Viologen Dichloride (98%) and Methyl Viologen Dichloride (98%) and Anhydrous Acetonitrile (99%) were purchased from ALDRICH, while Sodium Perchlorate (> 97%) was purchased from BDH Chemicals, Ltd and Potassium Carbonate Anhydrous from FROTAROM (UK), Ltd. All chemicals were used without further purification except methyl viologen dichloride, which was converted into methyl viologen perchlorate to increase its solubility by dissolving methyl viologen in H₂O. Excess of 70% HClO₄ was added dropwise. The resultant off-white precipitate was recrystallized once from CH₃OH/Et₂O and once from H₂O^[19].

Tetrabutylammonium perchlorate (TBAP) was prepared by modifying the published procedure. Schiff base crown ether was prepared as described in^[20].

Instrumentation

The electrochemical measurements were conducted using GAMRY instrument, Series G300 potentiostat / Galvanostat / ZRA Quick-Start Guide. Voltammetry cell was used with a platinum-rod working electrode, a silver/silver chloride (Ag/AgCl) reference electrode and a platinum-wire counter (auxiliary) electrode.

The following stock solutions were prepared: TBAP (0.100) M was prepared in anhydrous acetonitrile. Methyl viologen (3.318×10^{-3}) M was prepared using TBAP solution as a solvent. Benzyl viologen (1.120×10^{-3}) M was prepared using TBAP solution as a solvent. Crown ethers (1), (2), (3), (4), (5), (6), (7), (8) (6.636×10^{-2}) M were prepared using a methyl viologen solution as solvent or (2.241×10^{-2}) M using benzyl viologen solution as solvent. In every experiment, the concentration of viologen was kept constant.

Stock solutions of Schiff base crown ether (9) (1.269×10^{-2}) M were prepared using methyl viologen solution as a solvent or (1.824×10^{-2}) M using benzyl viologen solution as solvent. In every experiment, the concentration of viologen was kept constant. The working solution contains a constant volume of viologen solution

and variable amounts of crown ethers or Schiff base crown ether using a titration method. The cyclic voltammetry was recorded after each addition at room temperature (18-20 °C) and all solutions were deoxygenated by purging with dry nitrogen gas and maintained under an inert atmosphere during the electrochemical experiment. To the best of our knowledge, viologen solutions are stable at ambient temperature. It was noticed that viologen solutions are either colorless or yellow and the color of the complexes can also vary.

The cyclic voltammetric cell contains (5ml) of viologen solution, then a (0.1ml) increment of a crown ether or a Schiff base solution was added gradually. Cyclic voltammetry was studied for the first solution at different scan rates (50, 10, 150, 200, 250, 300, 400, 500 mV/s) and (0.05 mA) maximum current. The initial potential was (-0.15 V), scan limit 1 was (-1.2 V), scan limit 2 was (-0.15 V) and the final potential was (-0.15 V). The effect of light and oxygen was also studied on each complex solution after finishing the titration step.

Results

The cyclic voltammetry of the colorless (3.318×10^{-3}) M solution of MV was studied at different scan rates (50, 100, 150, 200, 250, 300, 400 and 500 mV/s), under nitrogen atmosphere at room temperature (18 - 20 °C).

Figure 1 shows the CV of MV at different scan rates; it shows two reversible waves corresponding to the redox couples. The half-wave potential ($E^{1/2}$) of the first reduction (-372.95 mV) and of the second reduction is (-778.45 mV). The ratio of cathodic (reduction) to anodic (oxidation) peak currents is nearly one. The peak to peak separation (ΔE_p) is equal to (~ 76 mV).

The positions of half-wave potential don't alter as a function of voltage scan rate, but the peak currents are directly proportional to the scan rates. This indicates that the potential waves are diffusion-controlled, since the reduced species diffused away from the electrode surface after receiving an electron from the electrode also as an indication of reversibility.

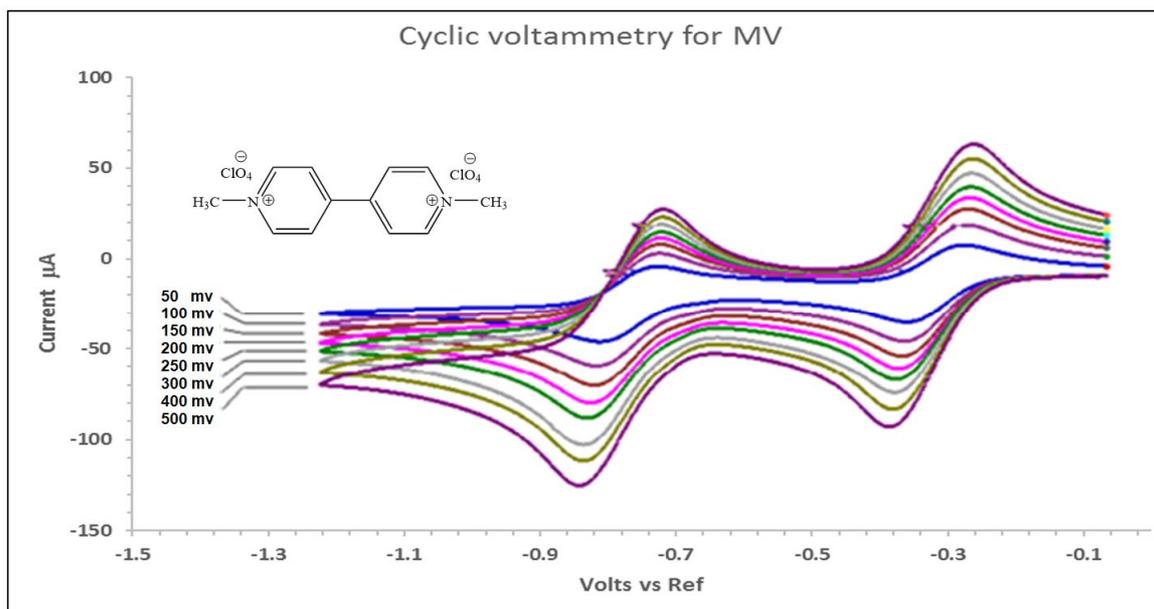


Figure 1. Cyclic voltammetry for MV (3.318×10^{-3} M) in the existence of TBAP (0.100) M, in anhydrous acetonitrile, at different scan rates, maximum current (0.05) mA and under room temperature (18-20) °C.

The migration of ions generates a current in the solution; so, when the applied voltage is increased, the movement of ions is also increased, thus the current is increased. This relationship is described by Randles-Sevcik equation:^[19]

$$I_p = (2.687 \times 10^5) n^{3/2} v^{1/2} D^{1/2} A C$$

Where,

I_p : The peak current (A).

n : The number of electrons appearing in half-reaction for the redox couple.

v : The scan rate (V / sec).

A : The electrode area (cm^2).

D : The analyte diffusion coefficient (cm^2/sec).

C : The concentration of analyte in bulk solution (mol/cm^3).

The constant is understood to have the units ($\text{C mol}^{-1} \text{V}^{-1}$).

The values of the scan rate and the cathodic peak currents obtained from CV curves of MV and the plots of the cathodic peak currents against the square root of the scan rate for the first electron transfer and second electron transfer show that the peak currents are directly proportional to the square root of scan rate. After careful substitution and unit analysis, the diffusion coefficient, D , of MV is equal to (3.618×10^{-3}) cm^2/s .

Complexation of Crown Ethers with Viologens

Complexation of crown ethers and viologens was studied using CV. The CV of viologen was recorded before adding the crown ethers under investigation. Increments of each crown ether were added and the CV was recorded after each addition at a scan rate of (100 mV/s), which is considered to be slow enough to maintain equilibrium concentration in the electrolyte solution. Potential values (E), peak to peak separation (ΔE) and half-wave potential ($E_{1/2}$) were recorded.

In this study, for each host, a figure that shows the CV of the viologen with different ratios of the host is presented, as well as a table that lists the values of ΔE , $E_{1/2}$, $\Delta E_{1/2}$ and $\text{Log} [\text{host}]$ for each ratio for the first electron transfer and second electron transfer.

Complexation of 1,10-diaza-18-crown-6 (4) with MV

The solution of 1,10-diaza-18-crown-6 (4) in MV solution is green under nitrogen, converts into yellow in the presence of oxygen and is dark orange under sunlight.

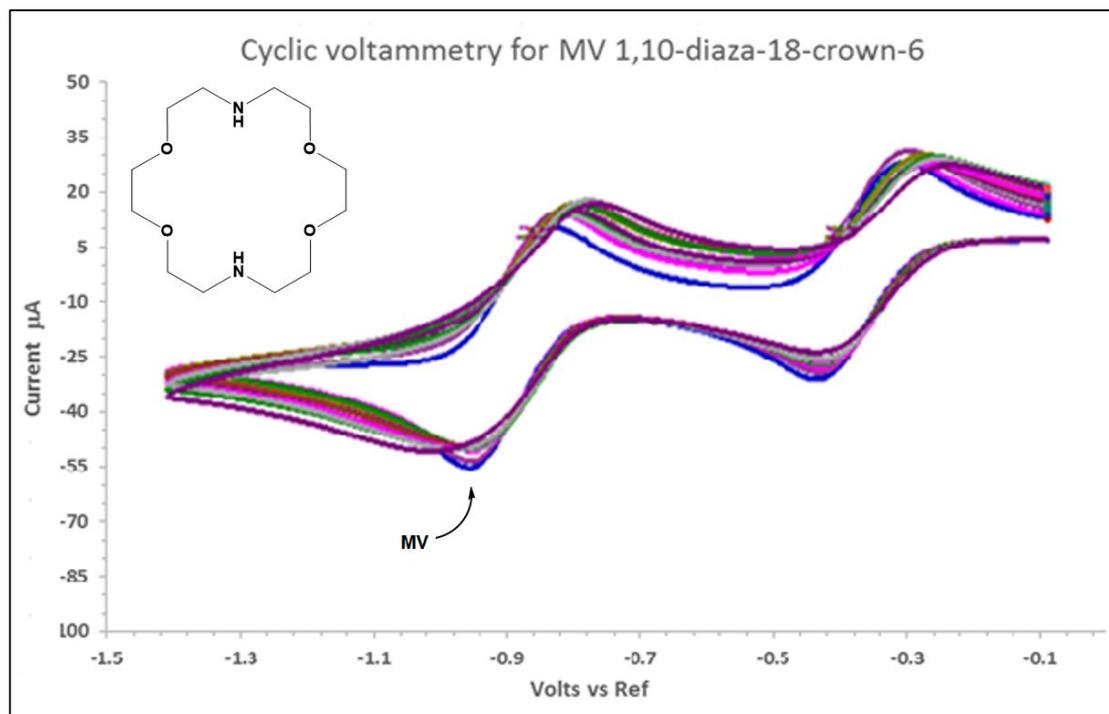


Figure 2. Cyclic voltammetry of MV (3.318×10^{-3} M) with a different concentration of 1,10-diaza-18-crown-6 (6.636×10^{-2} M) in the existence of TBAP (0.100) M, in anhydrous acetonitrile. Scan rate is (100) mV/s and maximum current is (0.05) mA, at room temperature (18-20 °C). The color of the solution is green.

Figure 2 shows a shift of the redox peak after each addition. Similar shift was observed with other hosts except for host (6), where the intensity of the two redox peaks decreased and a new peak appeared, which indicates the formation of a complex between MV and crown (6). This new peak is not part of host (6) CV.

Some of the hosts show positive shifts; others show negative shifts. The formation constant of each complex was determined from its shift using the modified form of Nernst equation, Eq.(1):^[21, 22].

$$(E^{1/2})_c = (E^{1/2})_s - (0.05916/n) \log K - (0.05916/n) p \log [\text{crown}] \dots\dots(1)$$

where; $(E^{1/2})_c$: the half-wave potential of cathodic wave of viologen in presence of crown.

$(E^{1/2})_s$: the half-wave potential of cathodic wave of viologen in absence of crown.

n: number of electrons involved in the reduction process.

p: ratio of crown to viologen.

Figures 3 and 4 show linear plots of Log [host] versus $\Delta E^{1/2}$ for first electron transfer and second electron transfer.

A plot of differences between half-wave potential ($\Delta E^{1/2}$) in presence and absence of the host versus log [crown 8] was obtained for the first electron transfer (Figure 3) and the second electron transfer (Figure 4). The plot is linear with a slope of $[-(0.05916/n)p]$ and an intercept of $[-(0.05916/n) \log K]$. The logarithm of formation constant value of each complex was obtained by dividing the intercept value over the slope value.

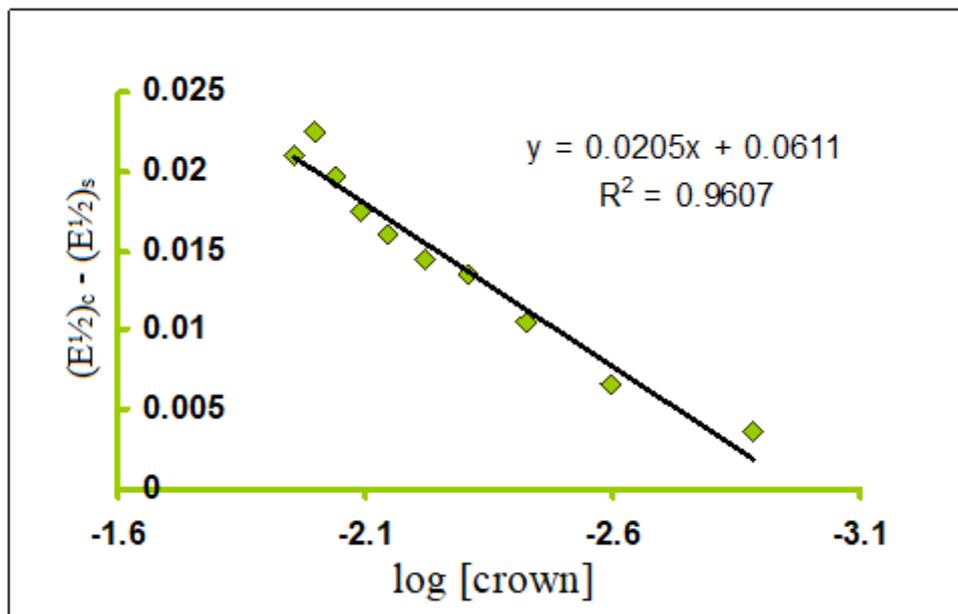


Figure 3. The plot of differences between half-wave potential ($\Delta E^{1/2}$) in presence and absence of crown (8) versus $\log [\text{crown}]$ for the first electron transfer.

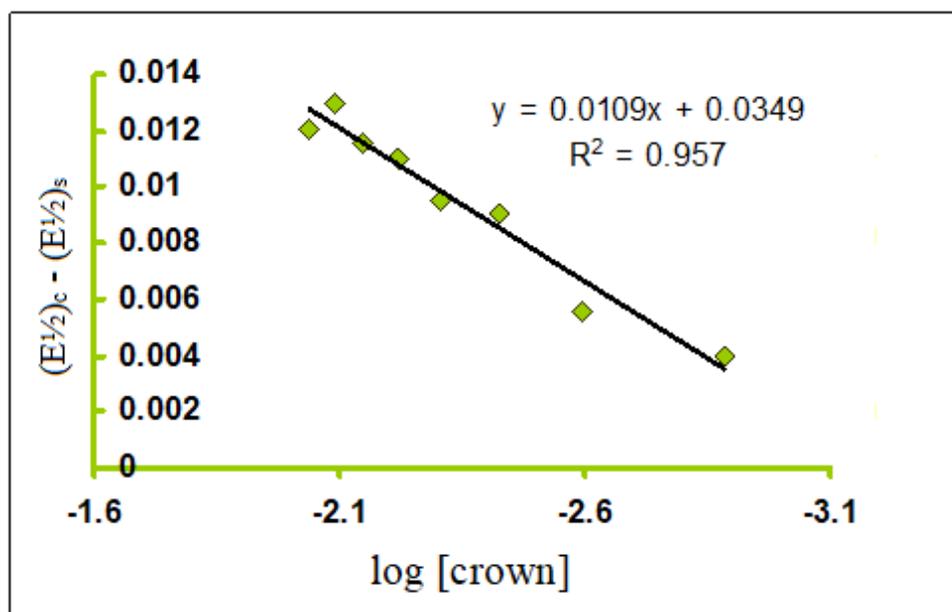


Figure 4. The plot of differences between half-wave potential ($\Delta E^{1/2}$) in presence and absence of crown (8) versus $\log [\text{crown}]$ for the second electron transfer.

Table 1. The peak to peak separation (ΔE) and half-wave potential ($E_{1/2}$) for each case for the first and second electron transfers.

$$V^{2+} \rightleftharpoons MV^+ \dots 1 \qquad MV^+ \rightleftharpoons MV \dots 2$$

Solution	Log[crown]	PP_1	$E_{1/2}(1)$	$\Delta E_{1/2}(1)$	PP_2	$E_{1/2}(2)$	$\Delta E_{1/2}(2)$
1	—	104.9	-371.55	0.00	101.0	-787.40	0.00
2	-2.89	107.8	-368.00	3.55	105.0	-783.40	4.00
3	-2.59	109.8	-365.00	6.55	107.9	-781.85	5.55
4	-2.43	113.9	-361.05	10.50	114.9	-778.35	9.05
5	-2.31	115.9	-358.05	13.50	118.0	-777.90	9.50
6	-2.22	121.9	-357.05	14.50	128.9	-776.35	11.05
7	-2.15	122.9	-355.45	16.10	127.9	-775.85	11.55
8	-2.09	127.9	-354.05	17.50	138.9	-774.45	12.95
9	-2.04	129.9	-351.95	19.60	142.9	-775.35	12.05
10	-2.00	135.8	-349.00	22.55	148.9	-777.45	9.95
11	-1.96	140.8	-350.50	21.05	159.8	-775.80	11.60
12	-1.72	144.0	-350.00	21.55	174.0	-789.90	-2.50
13	-1.60	155.0	-345.50	26.05	197.0	-785.50	1.90
Log $K_{(1)}$ =				2.98	Log $K_{(2)}$ =		3.20

PP_1 : peak to peak separation for the 1st electron transfer & PP_2 : peak to peak separation for the 2nd electron transfer – both represent the potential difference in mV between the cathodic and anodic peak potentials measured at 0.1 V/s.

$\Delta E_{1/2}$ (1): change in the half-wave potential $E_{1/2}$ for 1st electron transfer & $\Delta E_{1/2}$ (2): change in the half-wave potential $E_{1/2}$ for 2nd electron transfer. PP_1 , $E_{1/2}(1)$, $\Delta E_{1/2}(1)$, PP_2 , $E_{1/2}(2)$ and $\Delta E_{1/2}(2)$ are all in mV.

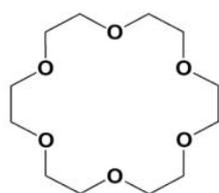
Log K values for the complexes that formed between viologens and different hosts are summarized in Tables (2) and (3) below.

Table 2. Log K values for the complexes formed between methyl viologen diperchlorate and different hosts.

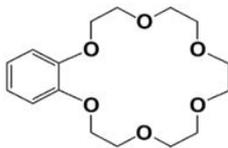
Complex	Log $K_{(1)}$	Complex	Log $K_{(2)}$
(1): MV^+	2.85	(1): MV	2.94
(2): MV^+	2.95	(2): MV	3.08
(3): MV^+	2.71	(3): MV	2.88
(4): MV^+	2.98	(4): MV	3.20
(5): MV^+	2.83	(5): MV	2.91
(6): MV^+	2.18	(6): MV	3.51
(7): MV^+	3.36	(7): MV	3.41
(8): MV^+	2.91	(8): MV	2.90
(9): MV^+	3.72	(9): MV	3.72

Table 3. Log K values for the complexes that formed between benzyl viologen dichloride and different hosts.

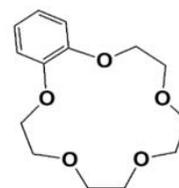
Complex	Log $K_{(1)}$	Complex	Log $K_{(2)}$
(1): BV ⁺	3.23	(1): BV	3.38
(2): BV ⁺	2.93	(2): BV	3.05
(3): BV ⁺	3.12	(3): BV	2.90
(4): BV ⁺	3.52	(4): BV	3.31
(5): BV ⁺	3.38	(5): BV	3.28
(6): BV ⁺	3.34	(6): BV	3.01
(7): BV ⁺	3.75	(7): BV	3.65
(8): BV ⁺	3.22	(8): BV	3.40
(9): BV ⁺	3.62	(9): BV	3.50



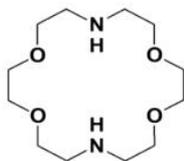
18-crown-6
(1)



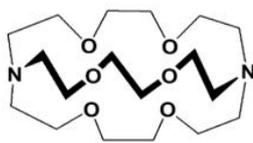
benzo-18-crown-6
(2)



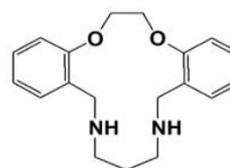
benzo-15-crown-5
(3)



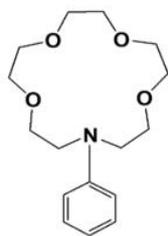
1,10-diaza-18-crown-6
(4)



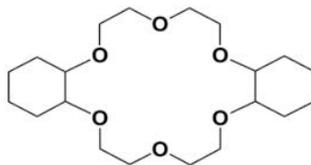
[2,2,2]cryptand
(5)



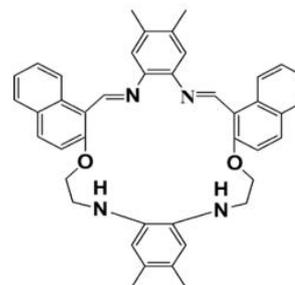
dibenzo-diaza-15-crown-4
(6)



phenylaza-15-crown-5
(7)



dicyclohexyl-18-crown-6
(8)



schiff base
(9)

Discussion

The results listed in Tables (2) and (3) show the Log K values of the complexes formed between methyl viologen diperchlorate (**MV**) and benzyl viologen dichloride (**BV**) and hosts used in this study.

The Log K values depend on several factors; some of these factors, such as the size of the cavity of the ligand and the number and nature of the donor atoms in the ligand, are important in the stability of the formed complexes. In addition to that, the substituents on the host and the flexibility of the host ring also affect the stability of the complexes.

Complexes of MV with Nitrogen-Oxygen Hosts

MV readily forms stable complexes with different hosts. It forms complexes with the hosts used in this study and the stability of the complexes varies according to the factors mentioned above. The values of Log K for the complexes formed between methyl viologen diperchlorate and those hosts are summarized in Table (2).

The values of Log K (around 3) for methyl viologen are in excellent agreement with the literature, although UV-visible spectrophotometry was used in determining the binding constant^[23].

Hosts (3), (6) and (7) all have 15-membered cavity size. They all differ in number (type) of donor atoms. Hosts (6) and (7) have nitrogen and oxygen hetero-atoms. On the other hand, host (3) has only oxygen hetero-atoms. Host (6) has only four hetero-atoms; this explains why the complex of MV with host (6) has the lowest log K value indicating that the most significant factor is the number of donor atoms of the ligand. The complex of MV with host (3) has a lower Log K value than with host (7). This is due to the presence of a nitrogen atom, which has a better donating ability over an O atom.

Hosts with larger cavity size and higher number of oxygen or nitrogen atoms have a stronger interaction and higher Log K values. A similar observation was reported previously^[24]. Both Log K values for the first and the second electrons have the same trend.

The other four hosts have almost the same 18-membered cavity size, but are different in electron density. The complexation study of

methyl viologen with 18-crown-6 (1), benzo-18-crown-6(2), 1,10-diaza-18-crown-6 (4) and dicyclohexyl-18-crown-6 (8) shows that the Log $K_{(1)}$ values increase in the order of (2) > (8) > (1), although the three hosts have almost the same cavity size. But owing to the cavity electron donating groups (phenyl or dicyclohexyl), hosts (2) and (8) have a higher donor ability than host (1); therefore, hosts (2) and (8) are expected to have a stronger interaction with MV than host (1). As we previously mentioned, nitrogen-containing hosts form more stable complexes than hosts without nitrogen atoms having the same size. Although hosts (7) and (3) have the same cavity size and both have a benzene ring, the Log K values of host (7) is higher than that of host (3). The same argument is applied to hosts (1) and (4), both of which have 18-membered cavity and six hetero-atoms; in addition, host (4) has two nitrogen atoms among them. This explains the higher stability of the complex formed between MV and host (4) over that formed between host (1) and MV.

Uncharged methyl viologen (**MV**) also forms complexes with hosts (1), (2) and (8) with Log $K_{(2)}$ values decreasing in the following order of (2) > (1) > (8). This order is the same as the Log $K_{(1)}$ above. The Log K values of hosts (1) and (2) with MV for the first electron transfer are less those for the second electron transfer. This observation indicates that those hosts bind MV in the following order of MV > MV⁺ > MV²⁺. Matsue *et al.* reported a similar trend for the complexation of MV with cyclodextrins,^[16] On the other hand, the Log K values of hosts (1), (2) and (3) with MV at the first electron transfer are lower than at the second electron transfer. This observation indicates that these hosts bind the methyl viologen in the order of MV > MV⁺ > MV²⁺.

On the other hand, host (8) has almost similar values for Log $K_{(1)}$ and Log $K_{(2)}$, which means that it has no recognition for any of the species. This order is reversed in the case of inclusion of methyl viologen in cucurbit[7]uril, where the association rate constants for the complexations were taken as $k_a = 4 \times 10^7$ (MV²⁺), 1×10^5 (MV⁺) and 7×10^2 (MV⁰) M⁻¹·s⁻¹.¹³ The voltammetric results clearly demonstrate that CB[7] prefers the

charged species such as MV^{2+} and MV^{1+} over the neutral species MV^0 as a guest.

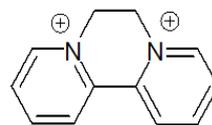
Host (5) is bicyclic; its cavity size is almost the same as that of host (4), while host (9) has a 20-membered cavity size with six hetero-atoms, four of which are nitrogen atoms. Thus, the stability of its complexes is expected to vary according to these factors.

Table (2) reveals that $\text{Log } K_{(1)}$ values increase in the order (9) > (7) > (4) > (5) > (6). In spite of the "cryptand effect", the $\text{Log } K$ value of the bicyclic host (5) is less than that of the monocyclic host (4) which also has two nitrogen atoms. Although crown (5) is bicyclic member, but it seems that its cavity is not ready for complexation. It is less accessible than the cavity of host (4) and needs preorganization. The monocyclic host (4) is more accessible than the bicyclic host (5), which causes $\text{Log } K$ value to be lower in the case of bicyclic host. Host (9) has the highest $\text{Log } K$ value among these hosts. It has a larger cavity size with four nitrogen atoms and has additional naphthyl and phenyl groups attached to the cavity, which cause $\text{Log } K$ value to be higher. The $\text{Log } K$ values of host (7) are higher than that of host (4), although host (7) has smaller cavity size than that of host (4). In this case, it seems that the cavity size and the number of hetero-atoms are not significant factors. We think that in this case the orientation of the hetero-atoms plays an important role; compound (4) is highly flexible and adopts several orientations, while compound (7), which has a phenyl group, would enhance electron donation and is less flexible and has fewer numbers of orientations, which helps have a stronger attraction with MV . In addition to that, an extra π - π interaction between the phenyl group on host (7) and aromatic groups of MV provides extra stability to the complexes.

Except for host (9), all nitrogen-containing hosts have $\text{Log } K_{(1)}$ values less than those of $\text{Log } K_{(2)}$ values, which means that those hosts bind MV species in the following order: $MV > MV^{+} > MV^{2+}$, while host (9) has no recognition among MV species; it binds them in the same order.

The $\text{Log } K$ values obtained in this study are comparable to $\text{Log } K$ values obtained from our work using UV-Vis^[16]. Jeon *et al.* studied the formation of 1:1 host-guest complex between methyl viologen and cucurbit[8]uril (CB[8]) in water. They reported the formation constant to

be $1.1 \times 10^5 M^{-1}$. In the presence of CB[8], two additional redox waves were observed beside the ones for free MV^{1+} . Chunlin *et al.* also reported the formation constant of 1:1 complexes between *cis*-dibenzo-30-crown-10 with paraquat to be $1.1 \times 10^3 M^{-1}$ and with diquat, shown below, to be $5 \times 10^4 M^{-1}$ ^[25].



Diquat

Tomokazu *et al.*^[17] studied the complexation of methyl viologens and cyclodextrins. The addition of β -CD results in the shift in the half-wave potential for the second electron transfer to the positive direction, whereas the first one showed only small potential changes. This observation indicates that β -CD binds the species in the following order: $MV > MV^{+} > MV^{2+}$.

Complexes of BV

The complexation of BV with the hosts mentioned previously is studied and the values of $\text{Log } K$ for the complexes formed between BV and those host molecules are determined. In all cases, the complex formation is associated with a shift of half-wave potential toward a negative or positive direction and a change in the peaks' intensities.

The values of $\text{Log } K$ for the BV complexes with the hosts under investigation are summarized in Table (3). $\text{Log } K_{(2)}$ values are consistent with what we previously mentioned; the smallest cavity size host (3) has the lowest stability complex. Host (2) has lower $\text{Log } K_{(2)}$ than expected. We believe that oxygen atoms forced to adopt improper orientation by the phenyl ring. This pre-orientation reduces the complexation ability of host (2).

Table (3) reveals that host (6) has the lowest $\text{Log } K_{(2)}$ values among the other hosts. Host (6) has only four hetero-atoms compared with the others which means that the number of donor atoms is a significant factor. BV interacts with nitrogen and oxygen atoms without being included in the cavity. In addition, the benzyl group of BV might interact with the two fused benzene rings of crown (6) via π - π interactions. The intensity of the two redox peaks in Figure (3) decreases and a new peak appears, which indicates the formation of a complex between BV and crown (6). The $\text{Log } K$ values of host (5) are lower than those of host (4). This observation

is similar to what we stated about **MV**, presumably due to the same reasons. It is also observed that Log *K* values of host (**9**) are higher than those of hosts (**4**), (**5**) and (**6**). This could be due to the increased number of nitrogen donor atoms of host (**9**), in addition to naphthyl and phenyl groups which provide extra binding sites and enhance the stability. The Log *K* values of host (**7**) are the highest although its cavity size is the smallest. This result might be explained depending on the 3-D structure of host (**7**). The structure has the phenyl ring almost perpendicular to the plane of the cavity. This will allow **BV** to form an inclusion complex and cause the phenyl groups of **BV** to have a π - π interaction or π -cation interaction with the phenyl of host (**7**).

The Log *K* values of all nitrogen-containing hosts, with **BV** at the first electron transfer, are higher than those at the second electron transfer. This observation indicates that those hosts bind **BV** in the order of $BV^{2+} > BV^{+} > BV$.

Generally, nitrogen-containing hosts form more stable complexes with **BV** than oxygen-containing hosts. This is due to the higher donocity of nitrogen atoms over oxygen atoms. Kuwabara *et al.* studied the charge transfer

complex between Benzyl viologen (**BV**) and *p*-benzocrown ether in acetone and found that the binding constant is about 200 M^{-1} using UV-Vis analysis^[26].

Conclusions

In general, complexes with **BV** are more stable than those with **MV**, having higher Log *K* values. Also, it is noticed that the hosts with aromatic substituents have higher Log *K* values with **BV** than those with **MV**. This is due to the addition of π - π interactions between the benzyl groups of **BV** and the aromatic rings in the hosts. The charge transfer complexes with aza-crown ethers are more stable than others.

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