

A thermodynamic study of the charge transfer complexes of MV with some macrocyclic hosts

Shehadeh A. Mizyed · Mohammad K. Shehab ·
Deeb S. Marji

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Abstract Formation of charge transfer complexes of methyl viologen, MV, and hosts (1–3) in ethanol were studied using UV–visible spectrophotometry. The stability constants and the thermodynamic parameters of the resulting 1:2 (MV:host ratio) complexes were determined. All charge transfer complexes formed were enthalpy destabilized, but entropy stabilized. The effect of donor atoms, their orientation, the substituents, flexibility and the cavity size of the crown ethers on the formation constants and thermodynamic parameters will be discussed.

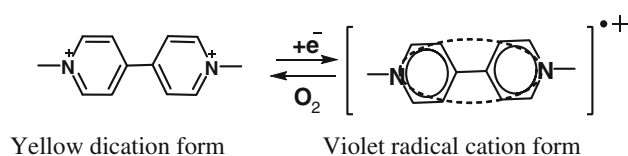
Keywords Charge transfer complexes · Methyl viologen · Stability constants · Crown ethers

Introduction

Crown ethers are cyclic polyethers containing repeating units of $-\text{CH}_2\text{CH}_2\text{O}-$ and may include heteroatoms like nitrogen, sulphur, phosphorus or silicon instead of, or as well as, oxygen (http://en.wikipedia.org/wiki/Crown_ether). The bicyclic rings with two points connected by at least three bridges, called cryptands [1, 2]. Crown ethers as hosts, have various cavity sizes and donating atoms (heteroatoms), they form complexes with different guests, such as metal ions, [60]fullerene (C_{60}) and viologens [3].

Viologenes, Fig. 1, are well known as electrochromic compounds, which owe their names to color changes from yellow dication form to violet radical cation form under the exposure of photo source (sun light) and return to dication

form when oxygen is available as shown by the equation below [4].



This radical cation represents one of the most stable organic radicals due to the delocalization of the radical electron between the two rings.

Viologens have important applications in optical activity, herbicidal activity and as an electron relay in photochemical systems designed for solar energy conversion [5]. However, the disadvantage of their charge transfer complexes is their instability in solution [6, 7].

Only few studies on the complexation of methyl viologen with crown ethers were published; Travis et al. [8] studied the charge transfer complex of dibenzo-24-crown-8: paraquat in acetone. They obtained experimental evidence for the formation 2:1 complex by using three-dimensional UV/visible Job's plot. Ashton et al. [9] reported the formation of 1:1 inclusion complex between *p*-benzocrown ether and methyl viologen in acetone (Scheme 1); they noted that the binding constants of inclusion benzyl viologen with *p*-benzocrown ether are smaller than that of methyl viologen. This might be due to the steric hindrance of benzyl group in benzyl viologen [10].

Cucurbit[8]uril (CB[8]) is a fascinating synthetic receptor due to its remarkable binding behavior of the host. Joen et al. [11] studied the formation of a 1:1 host-guest complex between MV^{+2} and CB[8] in water. All enthalpy changes (ΔH_f°) and entropy changes (ΔS_f°) for the

S. A. Mizyed (✉) · M. K. Shehab · D. S. Marji
Chemistry Department, Yarmouk University, Irbid, Jordan
e-mail: z79sam@hotmail.com

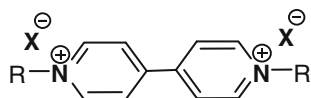
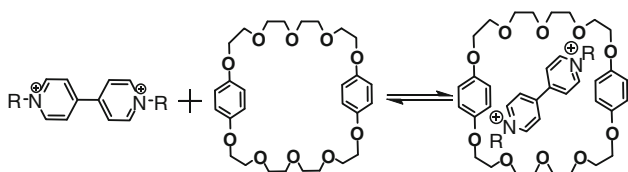


Fig. 1 General structure of viologens



Scheme 1 Schematic representation of complexation of viologen and *p*-benzocrown ether

complex formation of crown ethers with MV are positive, indicating an endothermic, entropy favored process. Typically, the complexation processes are accompanied with loss of entropy, this loss is minimum in the cases where the interaction between the host and the guest is weak; as in the case of MV with crown ethers (**1–3**). A weak host guest interaction results in an enthalpy disfavored process. In addition, the weak host–guest interaction reveals that the solvated host and/or guest are more stable than the solvated complex, resulting in an entropy favored process.

In this study we aim to report a detailed thermodynamic study of the complexation process between hosts **1–3** and MV using UV–visible spectrophotometry (Fig. 2).

Experimental

All chemicals were used as received. Absolute ethanol (GFC Chemical), MV dichloride (98.0% Aldrich), and hosts (**1–3**) (>98.0–99.0 Fluka). The absorption measurements were conducted using “UV 2450-Shimadzu”

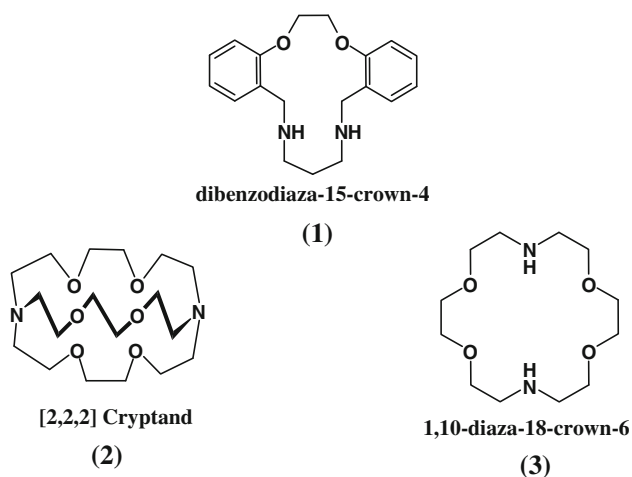


Fig. 2 The structures of hosts (**1–3**) under investigation

spectrophotometer connected to an electrical temperature controller was used to control the cell temperature up to ± 0.1 °C.

The concentration of MV was kept constant in each solution (4.00×10^{-5} M with host **1** and 2.00×10^{-4} M with hosts **2** and **3**), while the concentration of host **1** changes from 0.00 up to 4.00×10^{-4} M, and the concentrations of hosts **2** and **3** were changed from 0.00 up to 2.00×10^{-3} M. The stability constants were evaluated at different temperatures between 15 and 35 °C using Benesi–Hildebrand equation [12], the van't Hoff equation was applied to determine the thermodynamic parameters. Job's plot and mole ratio methods were used to determine the stoichiometry of the complexes [13].

Stock solutions of known concentrations (1.00×10^{-3}) M of host **1** and (5.00×10^{-3}) M of hosts **2** and **3** were prepared. Absolute ethanol was used as a solvent in all preparations. In our working solutions the concentration of MV was kept constant while the concentrations of the corresponding crown ethers varied up to 10 times the concentration of MV.

The absorbance measurements of these solutions were conducted against ethanol using a pair of matched quartz cells after leaving each solution for 3 days to ensure that it reached the equilibrium. The absorbances of the hosts stock solutions were measured to ensure that there is no absorbance in the visible region.

Results and discussion

When a colorless solution of each of hosts (**1–3**) in absolute ethanol was mixed with a colorless solution of methyl viologen (MV), a yellow color appears immediately. This change of color is due to the formation of a complex between MV and each of hosts (**1–3**). However, the existence of isosbestic points in the UV range gives additional indication for the formation of charge transfer (CT) complexes between MV and each of hosts (**1–3**). It is worth to mention that in all systems under investigation, the UV/Visible spectra were recorded after reaching equilibrium, each solution was left for 3 days to achieve this equilibrium. Figure 3 shows the absorption spectra of a series of solutions with different ratios of crown to MV, the new formed band and the isosbestic points are clearly shown.

This new band in the UV–visible region is clearly shown in Fig. 3, where neither host **1** nor MV absorbs in this region. The intensity of this band increases as the concentration of the crown ether increases. The same results were obtained with the other crown ethers **2** and **3**. Therefore, the appearance of isosbestic points indicates the

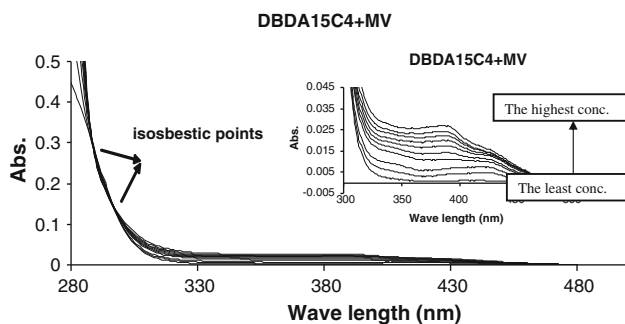


Fig. 3 Absorption spectra of MV ($4:00 \times 10^{-5}$ M) in the presence of host **1** in ethanol at 15 °C. The concentration of host **1** (from bottom to the top) 0.00 – $4:00 \times 10^{-4}$ M

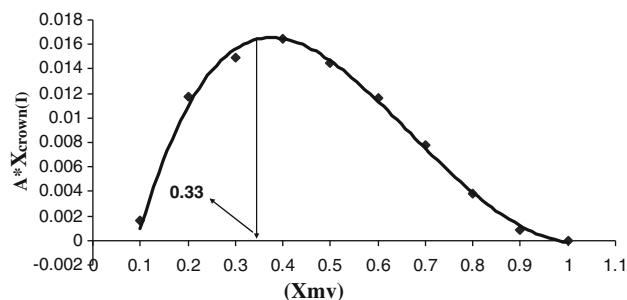


Fig. 4 Job's plot for the crown (**1**):MV complex in ethanol at $\lambda = 420$ nm

formation of a new species in the solution and formation of donor–acceptor complex.

The stoichiometry of the complexes of MV with crown ethers **1–3** under investigation was determined by using Continues Variation (Job's method). The stoichiometry of these complexes was found to be 2:1 (host (**1–3**):MV ratio) as shown in the Fig. 4.

Figure 4 clearly shows the existence of a maximum near 0.33, which means that a stable 2:1 crown (**1**):MV complex is formed.

The stability constant values, K_f , for the 2:1 complexes were determined using Benesi–Hildebrand equation specified for 2:1 ratio is shown in Eq. 1

$$\frac{[1]^2[MV]}{\Delta A} = \frac{[1]^2}{\varepsilon} + \frac{1}{\varepsilon \cdot K_f} \quad (1)$$

where [1] is the concentration of crown **1** (dibenzodiazia-15-crown-4), ΔA the absorbance change measured at 385 nm and ε is the molar extension coefficient.

When $\frac{[1]^2[MV]}{\Delta A}$ is plotted against $[1]^2$ gives a straight line with a slope of $\frac{1}{\varepsilon}$ and an intercept of $\frac{1}{\varepsilon \cdot K_f}$ is obtained, as shown in Fig. 5.

The thermodynamic parameters ΔH° and ΔS° of the CT complexes were obtained by applying the van't Hoff equation (2)

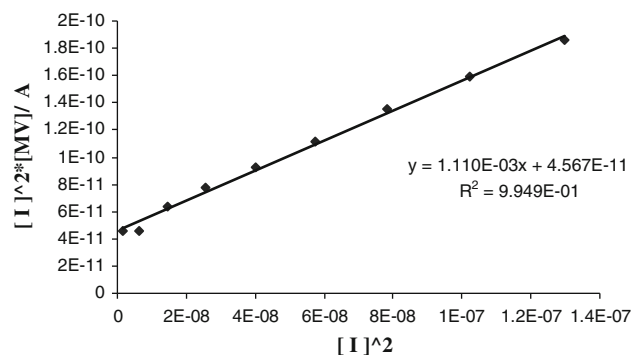


Fig. 5 2:1 Benesi–Hildebrand plot of crown (**1**):MV complex, in ethanol at 25 °C at $\lambda = 385$ nm

$$\ln K_f = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2)$$

A plot of $\ln K_f$ vs. $\frac{1}{T}$ gives a straight line with a slope of $-\frac{\Delta H^\circ}{R}$, and intercept of $\frac{\Delta S^\circ}{R}$. The values of ΔH_f° , ΔS_f° and ΔG_f° are listed in the Table 1. These values reveal that the stability constants of the complexes between MV and crown ethers **1–3** change as follows: dibenzodiazia-15-crown-4 > [2,2,2]Cryptand > 1,10-diazia-18-crown-6. Dibenzodiazia-15-crown-4 has the highest K_f value, this is probably due to the extra π -cation interaction caused by the fused benzene rings on the crown ether cavity with MV^{2+} dication. In addition to the interaction between the oxygen and nitrogen donor atoms with MV (Fig. 6).

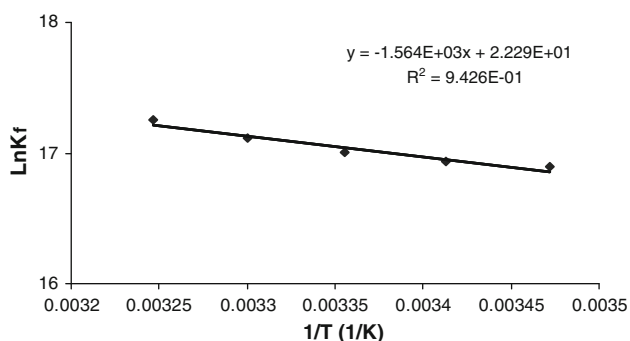
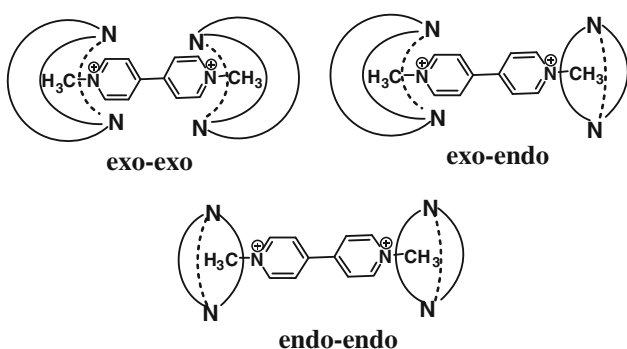
The small size cavity of dibenzodiazia-15-crown-4 and the fused benzene rings make it rigid and planar. Due to this planarity it is expected that MV can approach dibenzodiazia-15-crown-4 from either side leading to the formation of 2:1 aza-crown:MV complex. In the case of [2,2,2]Cryptand, it is expected that the MV can form endo–endo, endo–exo and exo–exo complexes that are shown in Fig. 7 [14, 15]. The presence of three maximum peaks in the absorption spectra of this complex is due to these possible conformations.

In the case of 1,10-diazia-18-crown-6, and due to its flexibility, the six donor atoms of the ring may lie in two planes, which are available to form complex with MV.

It should be noted that the formation of the complexes is spontaneous as indicated by the negative ΔG° values. The ΔH° values which measure the strength of the interaction between the hosts and the guest depend on number of binding sites, type of heteroatom, benzene rings, cavity size, and solvation. All enthalpy changes (ΔH°) for the complex formation of aza-crown with viologens are positive indicating that these reactions are enthalpy unfavored in ethanol solution. It is known that ethanol can strongly associate with aza-crown via hydrogen bonding as well as with viologens. This strong solvation with both host and guest will reduce their ability to form complexes. Entropy

Table 1 The thermodynamic parameters: ΔH_f° , ΔS_f° and ΔG_f° of complexes between crown ethers (1–3) with MV

Donor + MV	ΔH_f° (kJ/mol)	ΔS_f° (J/mol K)	$T\Delta S_f^\circ$ (kJ/mol)	ΔG_f° (kJ/mol)	Ln K_f 25 °C
Dibenzodiazia-15-crown-4	13.0 ± 0.6	185 ± 7	55.2	−42.2 ± 2.7	17.0 ± 0.8
[2,2,2]Cryptand	5.8 ± 0.3	154 ± 6	45.7	−39.8 ± 2.1	16.1 ± 0.8
1,10-Diaza-18-crown-6	11.4 ± 0.6	165 ± 7	49.1	−37.7 ± 2.7	15.3 ± 0.7

**Fig. 6** The van't Hoff plot for crown (1):MV complex in ethanol**Fig. 7** The three possibilities for inclusion MV with [2,2,2]Cryptand

change values are also affected by the change in the orientation and the interaction with the solvent molecules during the complexation. In typical host–guest studies, ΔS° values are used to be negative [16]. Formation of the complexes therefore results in a more ordered system, possibly due to the freezing of the motional freedom of both the guest and the host molecules. The ΔS° values in Table 1 are all positive, which favors the complex formation. This result could be due to the formation of less tight complexes and/or due to a solvophobic effect [17]. During formation of the complex, solvent molecules within the cavity of each host are displaced by MV molecule(s). It is proposed that upon complex formation with MV more solvent molecules are displaced. Thus, there is a larger entropy gain achieved from the displacement of solvent molecules. On the other hand, a less ordered state may also result due to the de-solvation of each of the host and MV of the solvent molecules them. This causes the solvent

molecules to have more freedom and increase the entropy of the process.

In conclusion the above results indicate that the complexation between viologens and aza-crown ethers are enthalpy unfavored and entropy favored which strongly depends on the solvation–desolvation of species.

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