A Thermodynamic Study of the Charge Transfer Complexes of C$_{60}$ with some Crown Ethers

Shehadeh A. Mizyed*, Deeb S. Marji and Enas Qarqaz

Chemistry Department, Yarmouk University, Irbid Jordan.

Received on Oct. 1, 2009 Accepted on Dec. 2, 2009

Abstract

Formation of charge transfer complexes of [60]fullerene, C$_{60}$, and crown ethers (1-4) in toluene was studied using Uv-Visible spectrophotometry. The stability constants and thermodynamic data of the resulting 1:1 complexes were determined. All charge transfer complexes formed were enthalpy stabilized, but entropy destabilized. The effect of donor atoms, their orientation, the substituents and the cavity size of the crown ethers on the formation constants and thermodynamic data are discussed.

Keywords: Charge transfer complexes; [60]Fullerene; Stability constants; Crown ethers.

Introduction

Crown ethers are macrocyclic ligands in which donor oxygen atoms are arranged in a ring, usually separated from each other by ethylene groups (-CH$_2$CH$_2$-). After their discovery by Pederson in 1967, crown ethers have undergone a remarkable development [1]. These compounds show interesting properties due to their ability to form stable inclusion complexes [2] with a number of inorganic salts, organic compounds and/or neutral molecules such as fullerenes [3]. It is worth to mention that crown ether-fullerene conjugates attracted substantial interest as advanced supramolecular materials and have found application in sensing devices for cations [3].

Most of the fullerenes supramolecular work was carried out with cyclodextrins [4] and calixerens [5]. Only few studies on the complexation of fullerenes with crown ethers have been carried out [6]. Complexation of fullerenes with electron donor molecules has been reported to change the fullerene physical and chemical properties [3]. In some inclusion complexes of fullerenes [6], charge transfer (CT) absorption bands were detected, from which significant information regarding the electron affinities of fullerenes and ionization potential of the host compounds as well as the stability of the complexes could be extracted.

* Corresponding authors: E-mail: z79sam@hotmail.com
Figure 1: The structures of crown ethers 1-4 used in this study

The complexation of C$_{60}$ with some selenacrown ethers in CCl$_4$ solution has been studied [6]. The values of formation constants were reported for 1:1 complexation that formed between C$_{60}$ with some selenacrown ethers as well as the thermodynamic data. All enthalpy changes ($\Delta H_f$) and entropy changes ($\Delta S_f$) for the complex formation of crown ethers with C$_{60}$ are negative, indicating that these complexation process are chiefly "enthalpy-driven" in CCl$_4$ [6]. The present study was carried out to study the thermodynamic of the charge transfer complexation of C$_{60}$ with crown ethers 1-4.

**Experimental**

Chemicals were used as received. Toluene (97.0% GCC), C$_{60}$ (99.5% Aldrich), and crown ethers (1-4) were used from Fluka (98.0-99.0%). The spectrophotometric measurements were conducted using a Unicam 100 double beam spectrophotometer, equipped with a home assembled thermostat cell holder (-10 and 80°C). A HAKK temperature controller was used to control the cell temperature with an accuracy of ±1°C.

The total concentration of [60]fullerene in each solution was 1.00x10$^{-4}$M, and the crown ethers concentration ranged from 0.00 up to 1x10$^{-3}$M.

Three runs were made for the calculation of each K value. The detailed procedure is reported elsewhere [7]. The stability constants were evaluated at various temperatures by using Benesi-Hildebrand equation [8]. The stoichiometry of the complexes was determined by using Job's plots and mole ratio methods [9].
Results and Discussion

When 0.02M solution of dibenzodiaza-15-crown-4 (1) is mixed with 1.00x10^{-4} M C_{60} solution in toluene, the magenta color of C_{60} solution changes to a yellow color. This change of color is due to the formation of a complex between C_{60} and dibenzodiaza-15-crown-4 \[^{[10]}\]. The change in C_{60} spectra due to the complex formation is shown in figure 2. This figure shows the spectra of C_{60} upon successive addition of small increments of dibenzodiaza-15-crown-4, this change in the spectra is due to the formation of a charge transfer complex. This figure also reveals the formation of a new band in the range of 400-450 nm, in this range non of the host or the guest shows any measurable absorption. Similar results were obtained with the other crown ethers used in this study. So the presence of this new band is due to the formation of donor-acceptor complexes between compounds (1-4) and C_{60} in toluene solution and not due to aggregation of C_{60}. This absorption has been seen by others on systems similar to ours \[^{[6, 9, 10]}\].

The stoichiometry of the complexes is determined by the Job's plots (continuous variation) method to be 1:1 (crown ethers-C_{60}) in all cases as shown in Figure 3. This figure shows a maximum near the mole fraction that represent the mole fraction of the host or the guest in the complex. This ratio was found at 0.5, indicating a 1:1 ratio for the dibenzodiaza-15-crown-4 to the C_{60} guest.

![Figure 2: Absorption spectra of C_{60} (1.00x10^{-4} mol/L) in the presence of 1, in toluene at 25^\circ C, the concentration of 1 (from bottom to the top): 0.00 to 7.89x10^{-3}(mol/L).]
Figure 3: Job’s plots for the C$_{60}$-1 complex in toluene, where $X_{C_{60}}$ represents the mole fraction of C$_{60}$.

The change in C$_{60}$ spectra with gradual addition of the donor was utilized to determine the formation constant by using the Benesi-Hildebrand equation which is shown in equation (1).

$$\frac{[A_o]}{\Delta A} = \frac{1}{([D_o].\varepsilon.K_f)} + \frac{1}{\varepsilon} \quad \text{..................................................(1)}$$

Where $[A_o]$ is the initial concentration of C$_{60}$, $[D_o]$ is the concentration of the crown ethers, $\Delta A$ is the absorbance change due to addition of crown ethers, and $\varepsilon$ represents the molar extinction coefficient of C$_{60}$-crown ethers. The plot of $[A_o] / \Delta A$ vs $1/[D_o]$ gives a straight line. The value of $K_f$ is calculated from the y-intercept value, which is equal to $1/\varepsilon$, and the slope value, which is equal to $1/\varepsilon.K_f$. Figure 4 shows a plot of $[A_o] / \Delta A$ against $1/([\text{dibenzodiaza-15-crown-4}])$, which confirm the 1:1 stoichiometry. The calculated formation constants are listed in table 1.

Determining these constants at different temperatures allows for the use of the van’t Hoff equation (Equation 2) and determine the thermodynamic parameters $\Delta H^0$ and $\Delta S^0$ of the charge transfer complex. The plot of $\ln K_f$ vs $1/T$ gives a straight line with a slope of $-\Delta H^0/R$ and $\Delta S^0/R$ as the y-intercept.
Figure 4: A typical Benesi-Hildebrand plot of C\textsubscript{60}:1 complex, in toluene at 25\degree C  
\[ \ln K_f = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]  

Figure 5 shows a plot of \(\ln K_f\) vs 1/T for the C\textsubscript{60}:1 complex. The enthalpies and entropies of the complexation process are summarized in table 1.

Table 1: The thermodynamic parameters and formation constants for different crown ethers-C\textsubscript{60} complexes in toluene solution.

<table>
<thead>
<tr>
<th>Donor</th>
<th>(\Delta H^\circ) (kJ/mol)</th>
<th>(\Delta S^\circ) (J/mol.K)</th>
<th>T(\Delta S^\circ) (kJ/mol)</th>
<th>(\Delta G^\circ) (kJ/mol)</th>
<th>Log (K_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-38.1 ± 0.8</td>
<td>-87.2 ± 2.7</td>
<td>-25.9</td>
<td>-12.2</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>-46.3 ± 0.5</td>
<td>-117.5 ± 1.8</td>
<td>-35.0</td>
<td>-11.3</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>-34.9 ± 0.5</td>
<td>-86.4 ± 1.6</td>
<td>-25.7</td>
<td>-9.2</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>-61.1 ± 0.5</td>
<td>-174.9 ± 1.7</td>
<td>-52.1</td>
<td>-9.0</td>
<td>1.6 ± 0.1</td>
</tr>
</tbody>
</table>

Results in table 1, show the formation constants (\(K_f\)) between C\textsubscript{60} and crown ethers decrease in the order of 1 > 2 > 3 > 4 knowing that, the formation constant values depend on several factors among them (1) type and number of donor atoms (2) the substituents on the crown ethers (3) and cavity size of the crown ethers. The above factors explain why crown 1 and 2 have larger formation constant than crown 3 and 4 since nitrogen atom is better donating than oxygen atom \[^{[11]}\]. A stronger interaction between crowns 1 and 2 with C\textsubscript{60} is expected. In addition the aromatic rings in crown 1 are expected to provide an extra stability to the complex formed between C\textsubscript{60} and crown 1 via \(\pi\rightarrow\pi\) interaction.
Previous studies between selenacrown ethers and C_{60} indicated similar π→π interactions between crown aromatic rings and C_{60} \cite{3}. The complex between crown 3 with C_{60} is slightly more stable than the analogous complex with crown 4. This could be due to a better orientation of the donating atoms in crown 3 as compared with crown 4 which leads to a stronger interaction between crown 3 and C_{60}. Oxygen atoms of benzo-18-crown-6 may be not completely available for complexation with C_{60}. For this reason, it is expected that formation constant of benzo-18-crown-6 with C_{60} is less than of benzo-15-crown-5 with C_{60}. Similar results were reported for dibenzo-24-crown-8 and benzo-15-crown-5 complexes with C_{60} in CCl_{4} \cite{5}.

The values of $\Delta H^o_f$ and $\Delta S^o_f$ for the complexes are also shown in table (1). As shown, the $\Delta H^o_f$ values are negative, as most of the typical host –guest complexation process, suggesting an "enthalpy-deriven" complexation. The $\Delta S^o_f$ values are negative, indicating that the complexation processes are unfavoured. It is known that $\Delta H^o_f$ values are related to the strength of the interaction between the donor and acceptor. The variation of negative enthalpies of C_{60}-crown ethers complexes decrease in the order crown 4:C_{60} > crown 2:C_{60} > crown 1:C_{60} > crown 3: C_{60}. This order suggests that the interaction between C_{60} and the crown ethers depend on the number of donor atoms. Both crown 4 and 2 contain six hetero atoms, which are larger than the others and hence -$\Delta H^o_f$ for these crown complexes are larger. Another factor that may affect the values of negative $\Delta H^o_f$ for C_{60} with crown 4 is the presence of aromatic ring, which enhances the π→π interaction between C_{60} and benzene ring in crown ethers. This factor is more pronounced than the role of the type of donating atom \cite{11,12}. The slightly difference in $\Delta H^o_f$ values for the complexes C_{60}-crown1 and C_{60}-crown3 is probably due to the stronger interaction between C_{60} and the aromatic ring in crown 1.
The entropy changes for complexation of crowns 1, 2, 3 and crown 4 are expected to vary with the size of crown ethers, as well as with the extent of crown ether-solvent interactions. The interaction of C\textsubscript{60} molecule with the flexible crown ether molecule results in the formation of a rigid charge transfer adduct in which the produced conformation of the two component molecules for maximum overlap will lead to negative \( \Delta S^o_f \) during the complexation reaction. This explains why \( \Delta S^o_f \) values for the complexes crown 2:C\textsubscript{60} and crown 4:C\textsubscript{60} have high negative \( \Delta S^o_f \) values than the complexes of 1 and 3 with C\textsubscript{60}.

The spontaneity of complexation is determined by the \( \Delta G^o_f \) values, this was determined according to Equation (3), and the values are listed in table (1)

\[
\Delta G^o = \Delta H^o - T\Delta S^o~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~(3)
\]

The values of \( \Delta G^o \) also can be correlated to log \( K_f \) values according to equation (2). Table (1) shows the trend in \( \Delta G^o \) values is as follows 1 \( > \) 2 \( > \) 3 \( = \) 4 and this is the same trend as log \( K_f \) values.

Table (1) shows that as the values of \(-\Delta H^o\) increase the values of \(-T\Delta S^o\) also increases, which follows the Enthalpy-Entropy compensation. To show this effect the data were fitted to equation (4)

\[
T\Delta S^o = T\Delta S^o_o + \alpha \Delta H~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~(4)
\]

A plot of \( T\Delta S^o_o \) vs \(-\Delta H^o\) gave a straight line with a good correlation coefficient was obtained and shown in figure (5). The intercept is \(-T\Delta S^o\) with value of -12.4 and a slop is \( \alpha \) with value if 1.04. these values suggest the entropies changes due to two components \[^{12}\]. The first component is independent on the enthalpy change \( (T\Delta S^o_o) \) and the second is proportional to \( \alpha \Delta H^o \). the proportionality factor, \( \alpha \), might be considered as a quantitative measure of the enthalpy–entropy compensation.

![Figure 6: A plot of \(-T\Delta S\) (kJ/mol) vs \(-\Delta H\) (kJ/mol) for crown ethers 1-4 with C\textsubscript{60}](image-url)
The negative intercept ($T\Delta S^\circ$) value indicates that the complex formation is not favored in the absence of an enthalpic contribution, emphasizing that the complex formation is entropy unfavored while it is enthalpy favored $^{[11, 12]}$.

In conclusion, crown ethers 1-4 used in this study formed stable complexes with $C_{60}$ under the experimental conditions. These complexes are enthalpy stabilized and entropy destabilized.

**Acknowledgements**

The authors would like to acknowledge Yarmouk University for financial support, Projects Numbers (5/2007) and (13/2007).

**References**


