

# A Thermodynamic Study of Charge Transfer Complexes of C<sub>60</sub> and Some Macrocyclic Ligands

## Research Article

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### Abstract

4 and Schiff base crown ethers 5 and 6 was studied in toluene using UV/Vis spectrophotometry at five different temperatures. The values of stability constant (Kc) for each complex were determined using Benesi-Hildebrand equation.

The obtained Kc values were found to depend on the cavity size, the macrocyclic effect and the substituents on the host. All complexes were found to have 1:1 stoichiometry as obtained by Job's plot method. In addition, the enthalpy and the entropy of complexation were estimated for all complexes. The complexation between C<sub>60</sub> and Ligands 1, 2 and 4 are enthalpy favored and entropy unfavored, while the complexation with 3, 5 and 6 are enthalpy unfavored and entropy favored.

**Keywords:** Charge transfer, C<sub>60</sub>, Stability constant, Macrocyclic ligand, Thermodynamic parameters.

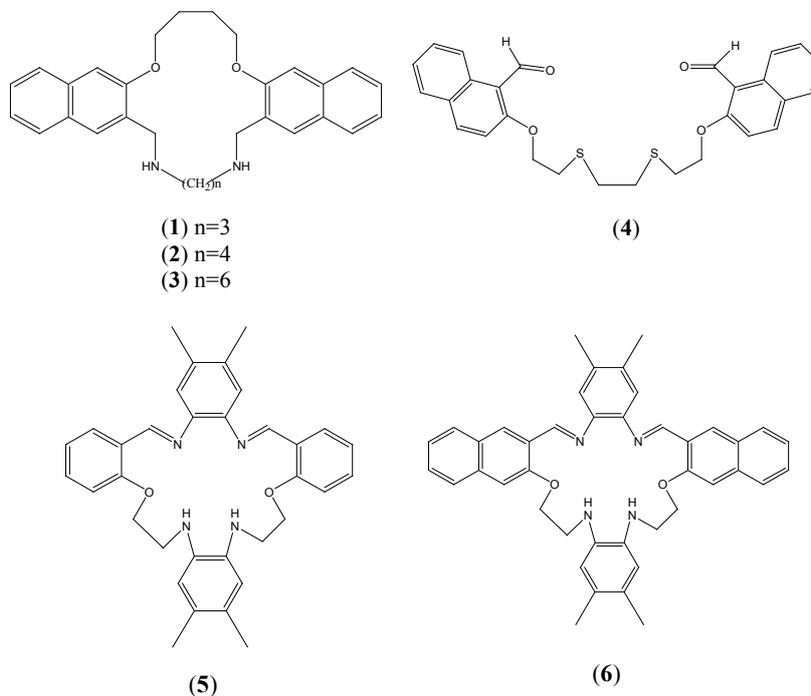
### Introduction

Macrocyclic Ligands are Polydentate cyclic compounds which contain donor atoms such as N, O, Se or S. These Ligands are very useful in supramolecular chemistry, as they provide suitable cavities that can completely surround different guest species including cations, anions or neutral molecules such as fullerene [1,2].

Fullerene (C<sub>60</sub>) is the third form of carbon after diamond and graphite. It was reported that C<sub>60</sub> forms charge transfer complexes with a variety of host systems such as calixarenes [3,4], crown ethers [5], amines [6] and cryptands. These complexes have wide applications in many technological fields, such as in non-linear optical materials, surface chemistry [7], solar energy storage [8] and semiconductors [9].

The complexations between C<sub>60</sub> and different types of crown ethers [10,11], thiocrown ethers [12] and selenacrown ethers [13] were extensively studied. The results of these studies show that C<sub>60</sub> formed 1:1 complexes with these crown ethers. Several factors were reported to affect the stability of these complexes including the type and number of donor atoms, as well as the substituents and the cavity size of the crown ethers. Several studies show that C<sub>60</sub> formed 1:1 or 1:2 Charge transfer complexes with calix[n]arene and calixarene derivatives [14,4].

The present study was carried out to synthesize ligand 4, resynthesize ligand 6 and study the thermodynamic parameters of the charge transfer complexation of  $C_{60}$  with the macrocyclic ligands 1-6.



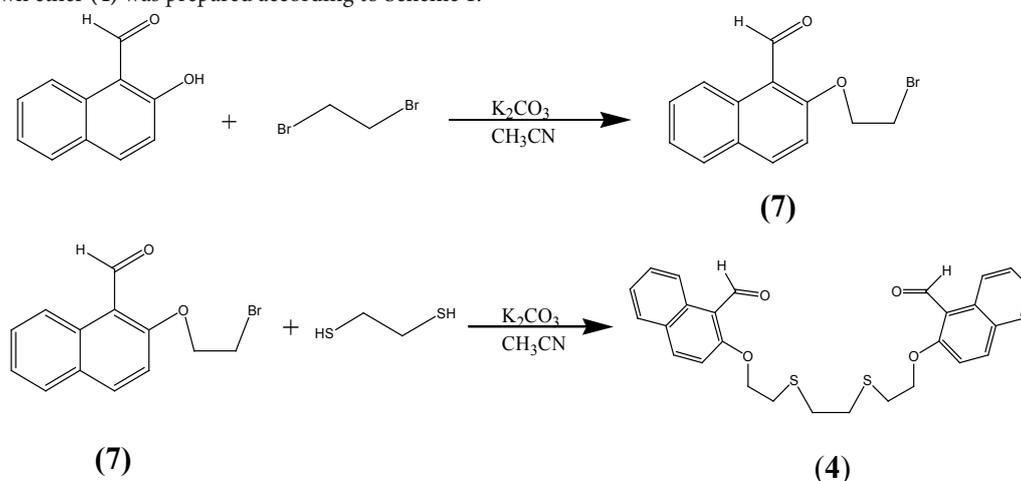
## Experimental

$C_{60}$  (99.0% Aldrich) and Toluene were used without any purification. Ligands (1-3, 5 and 6) were previously prepared according to the literatures [15,16,17].

The  $^1H$ -NMR and  $^{13}C$ -NMR spectra were recorded on 400 MHz and 100 MHz respectively, using Bruker Avance III. Melting points were determined using an electrothermal-digital melting point apparatus. Mass spectra were determined by VG-Analytical model 7070E. The absorption measurements were obtained using UV/Vis spectrophotometer "UV 2450-Shimadzu" connected to an electrical temperature controller with uncertainty  $\pm 0.1^\circ C$ .

### Preparation of compound (4)

Acyclic thiacrown ether (4) was prepared according to Scheme 1:



**Scheme 1:** The synthesis of acyclic (Podand) thiacrown ether (4)

Compound 7 was synthesized according to the previously published procedure [17]. The physical and spectroscopic data were similar to the published data [17].

In 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser, *o*-(2-bromoethoxy) naphthaldehyde 7 (0.82 g, 2.94 mmol), ethane-1,2-dithiol (0.12 ml, 1.47 mmol) and anhydrous  $K_2CO_3$  (0.41 g, 2.94 mmol) were mixed with anhydrous  $CH_3CN$  (60 ml). The mixture was refluxed for 24 hr under nitrogen atmosphere and then cooled to room temperature, filtered from residual  $K_2CO_3$ . Compound 4 was obtained as a solid product with an off-white color, m.p (147-148°C).

$^1H$ -NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 2.93 (4H, s,  $SCH_2CH_2S$ ), 3.06 (4H, t,  $J=6$ ,  $SCH_2CH_2O$ ), 4.41 (4H, t,  $J=6$ ,  $SCH_2CH_2O$ ), 7.26 (2H, d,  $J=7$ , ArH), 7.44 (2H,  $J=7$ , t, ArH), 7.64 (2H, t,  $J=8$ , ArH), 7.77 (2H, d,  $J=8$ , ArH), 8.03 (2H, d,  $J=8$ , ArH), 9.26 (2H, d,  $J=8$ , ArH), 10.94 (2H, s, CHO).

$^{13}C$ -NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 31.4, 33.0, 69.3, 113.5, 117.2, 124.9, 125.0, 128.3, 128.8, 130.0, 131.5, 137.6, 162.8, 191.9.

DEPT 135 ( $CDCl_3$ , 100 MHz) +ve: 113.5, 124.9, 125.0, 128.3, 130.0, 137.6, 191.9 . -ve: 31.4, 33.0, 69.3.

MS ( $m/z$ ) = 491  $M^+$ .

The concentration of  $C_{60}$  in each solution was kept constant at ( $1.33 \times 10^{-5}$  M with ligands 1-4 and  $1.00 \times 10^{-5}$  M with ligands 5 and 6). The concentration of the ligands changes from 0.00 up to  $5 \times 10^{-4}$  M. The stability constants were evaluated at different temperatures between 15 and 35°C using Benesi-Hildebrand equation. The thermodynamic parameters were determined using van't Hoff equation.

The stoichiometry of the complexes was determined using Job's plot method in which the total concentration of ligands and  $C_{60}$  is kept constant and the concentration of each is varied. Toluene was used as a solvent in all preparations.

Each solution was kept at the desired temperature for three days to attain the equilibrium. After that, the absorbance of each solution was measured against toluene using a pair of matched quartz cell.

## Results and Discussions

When a colorless solution of diaza crown ethers (1- 3) or acyclic crown ether 4 is mixed with violet  $C_{60}$  solution, the color changed to a pale yellow. This change in color of  $C_{60}$  may be due to the formation of charge transfer complexes between these ligands and  $C_{60}$ . However, when a solution of Schiff base crown ether 5 or 6 is mixed with  $C_{60}$  solution, the yellow color does not appear which is probably due to the low concentrations of  $C_{60}$  and these ligands in spite of the change observed in UV\Vis spectra.

The absorption spectra of a series of solutions with ratios from 0 to 20 of ligand 1 to  $C_{60}$  were shown in Figure 1.

Figure 1 reveals the formation of a new absorption band at wavelength  $\lambda=315$  nm, which shows blue and narrowing shifting of the peaks at  $\lambda=330$  nm. The same results were obtained with ligands 2 and 3.

The absorption spectra of a cyclic crown ether 4 shows the appearance of two new absorption bands at  $\lambda=306$  nm and 321 nm as shown in Figure 2. Several new bands in the range of 293-330 nm were observed in the absorption spectra of  $C_{60}$ : Schiff base crown ether 5 complex as shown in Figure 3.

The change in  $C_{60}$  spectra of the complex formation with Schiff base crown ether 6 is shown in Figure 4. This spectra shows the broadening of the peak at  $\lambda= 335$  nm.

The stoichiometries of all these complexes were found to be 1:1 using Job's plot method as shown in Figure 5. This figure shows a maximum ratio at 0.5, indicating a 1:1 ratio for the complexes.

The stability constant values,  $K_c$ , for the 1:1 complexes were determined using Benesi-Hildebrand equation 1:

$$[A_0]/\Delta A = 1/(\epsilon \cdot K_c \cdot [D_0]) + 1/\epsilon \dots\dots\dots 1$$

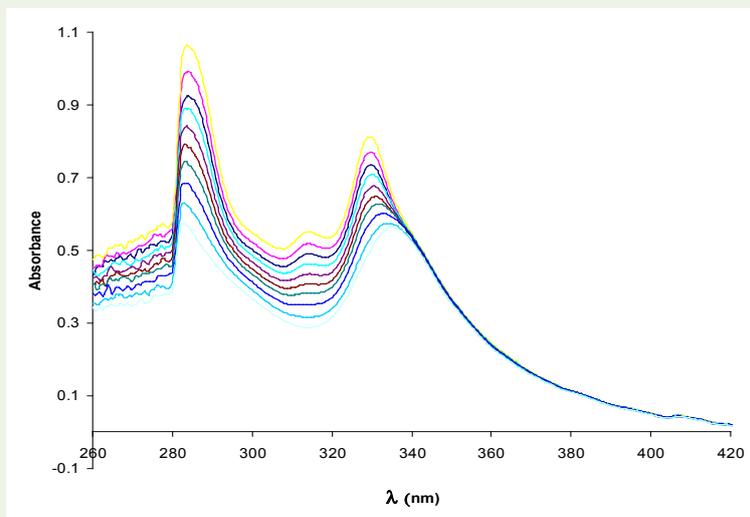
Where  $[A_0]$  and  $[D_0]$  indicate the initial concentration of A and D respectively,  $\Delta A$  the absorbance change and  $\epsilon$  is the molar extension coefficient. When  $[A_0]/\Delta A$  is plotted against  $1/[D_0]$  gives a straight line with a slope of  $1/\epsilon \cdot K_c$  and an intercept of  $1/\epsilon$  is obtained, as shown in Figure 6.

The thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  of the complex were obtained by applying the van't Hoff equation 2:

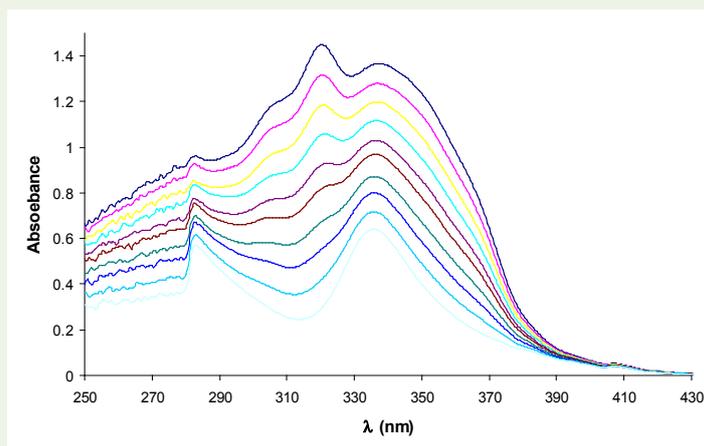
$$\ln K_c = -\Delta G^\circ/RT = -\Delta H^\circ/RT + \Delta S^\circ/R \dots\dots\dots 2$$

A plot of  $\ln K_c$  vs  $1/T$  gives a straight line with a slope of  $-\Delta H^\circ/R$ , and  $\Delta S^\circ/R$  as an intercept as shown in Figure 7. The values of  $\log K_c$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  are listed in the Table 1.

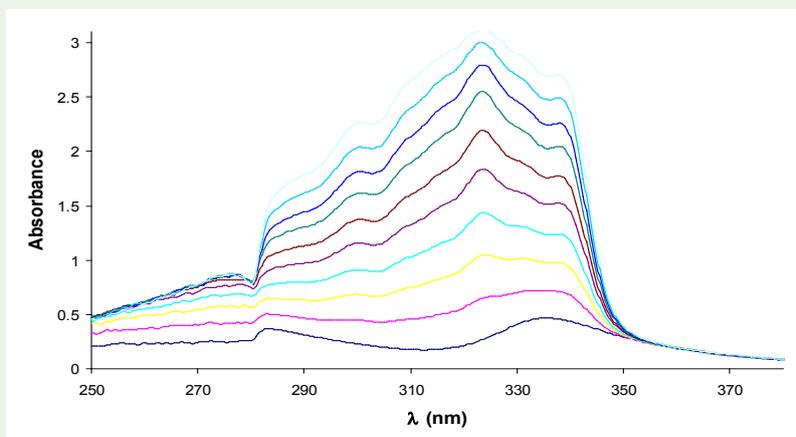
As shown in Table 1, the values of  $\log K_c$  between  $C_{60}$  and ligands 1, 2 and 3 decrease in order of  $2 > 1 > 3$ . This behavior of the ligands can be explained by considering the cavity sizes of the ligands. It seems that ligand 2 has a cavity that better fits  $C_{60}$  molecule while the cavity of ligand 1 is smaller and cavity of ligand 3 is larger than  $C_{60}$  molecules. Previous study on the complexation of these ligands with  $Ni^{+2}$  showed that



**Figure 1:** Absorption spectra of C60 ( $1.33 \cdot 10^{-5}$  M) in the presence of 1 in Toluene at 25°C.



**Figure 2:** Absorption spectra of C60 ( $1.33 \cdot 10^{-5}$  M) in the presence of 4 in Toluene at 25°C.



**Figure 3:** Absorption spectra of C60 ( $1 \cdot 10^{-5}$  M) in the presence of 5 in Toluene at 25°C.

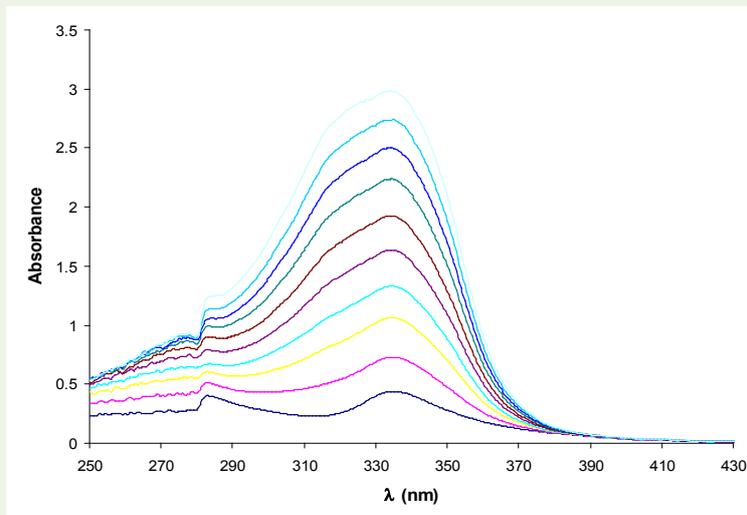


Figure 4: Absorption spectra of C<sub>60</sub> (1\*10<sup>-5</sup>) M in the presence of 6 in Toluene at 25°C.

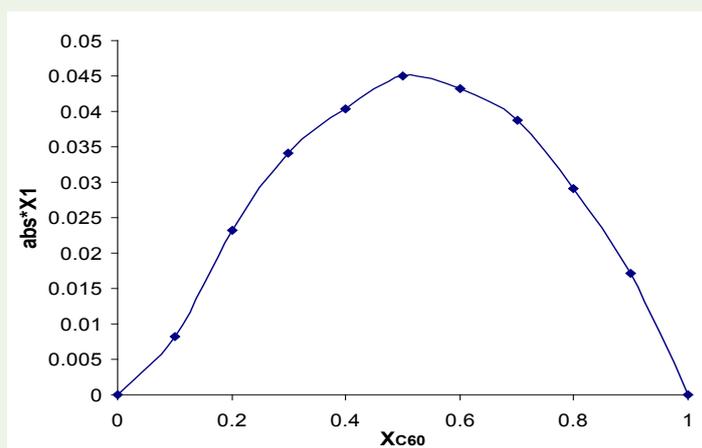


Figure 5: Job's plot for C<sub>60</sub>:1 complex in Toluene at 25°C.

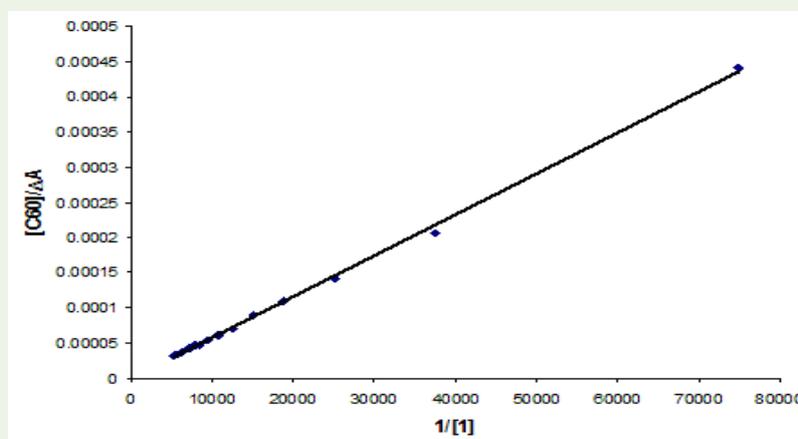


Figure 6: : A typical Benesi-Hildebrand plot of C<sub>60</sub>:1 complex in Toluene.

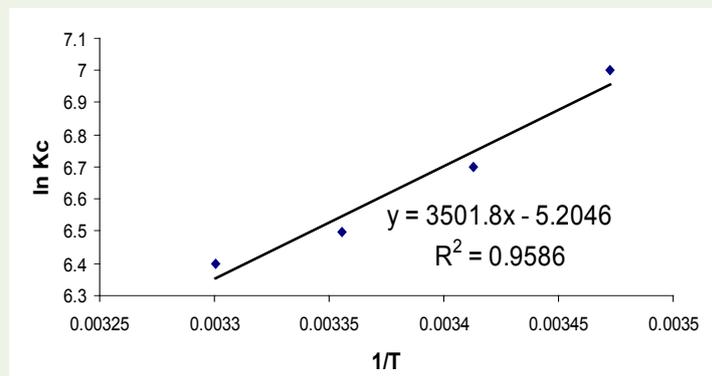


Figure 7: A plot of  $\ln K_c$  against  $1/T$  of  $C_{60}:1$  complex in Toluene.

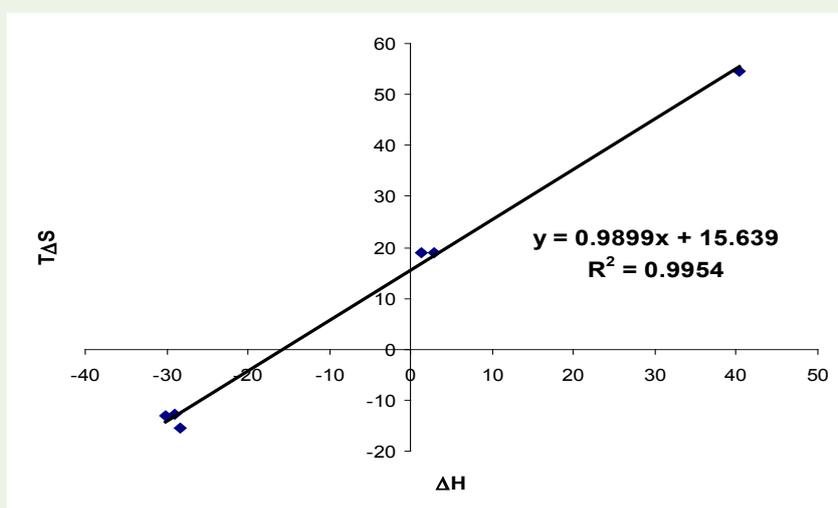


Figure 8: Enthalpy-Entropy Compensation Effect.

Table 1: The values of  $\log K_c$  and the thermodynamic parameters:  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the complexes.

Ligands	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	$T\Delta S^\circ$ (KJ.K/mol)	$\Delta G^\circ$ (KJ/mol)	Log $K_c$ at 25 °C
1	-29.11	-43.27	-12.89	-16.22	2.84
2	-30.13	-43.62	-12.99	-17.14	3.07
3	40.39	182.76	54.46	-14.07	2.44
4	-28.42	-52.22	-15.56	-12.86	2.25
5	2.82	63.53	18.93	-16.11	2.83
6	1.19	63.95	19.06	-17.87	3.13

Table 2: Slope  $\alpha$  and intercept  $T\Delta S^\circ$  for 1:1 complexations with various ligands.

Ligands	A	$T\Delta S^\circ$
1-6	0.99	15.64
Thiacrown ethers with $I_2$	0.98	12.6
$K^+$ 18-crown-6	0.86	2.4
$K^+$ Bis-crown ether	1.03	4.6
Podand	0.86	2.3

the complexes stabilities follow the sequence:  $1 > 2 > 3$ . This was explained depending on the cavity size matching too [16]. Since ligand 1 has smaller cavity size than 2, it formed a less stable complex with  $C_{60}$  resulted from the miss matching between the cavity size of 1 and  $C_{60}$ . Ligand 3 has the weakest interaction with  $C_{60}$ , this is probably due to that it has larger cavity size than 1 and 2 and more flexible than both, this flexibility requires preorganization step which needs a lot of energy to occur, also the orientation of the nitrogen atoms in the ring may be unsuitable for the complexation. Also,  $C_{60}$ :4 complex has the lowest value of  $\log K_c$ , probably due to the "Macrocyclic Effect" which states that a macrocyclic ligand complex is more stable than its open chain analogue.

The charge transfer complex of  $C_{60}$ :6 is more stable than that of  $C_{60}$ :5 as evidenced by larger  $K_c$  value. This is probably due to the presence of naphthyl group which afford extra binding sites for  $\pi$ - $\pi$  interaction in comparison with phenyl group in 5.

The results in Table 1 also show that ligands 1, 2 and 4 have negative values of  $\Delta H^\circ$  which indicate that these complexations are exothermic and enthalpy favored in toluene. However,  $\Delta S^\circ$  values are negative indicating that these processes are endothermic and entropy unfavored. Considering ligands 3, 5 and 6, both  $\Delta H^\circ$  and  $\Delta S^\circ$  values are positive and relatively high, which indicates that the complexation between  $C_{60}$  and these ligands are enthalpy unfavored but entropy favored. It is known that when having stable complexes with strong interactions, formation of these complexes is enthalpic favored and entropic disfavored and vice versa.

### Enthalpy-Entropy compensation effect

Table 1 shows that the values of  $\Delta H^\circ$  are correlated to the values of  $\Delta S^\circ$  and the regression of the equation 3 shows a good correlation when  $T\Delta S^\circ$  is plotted against  $\Delta H^\circ$  as shown in Figure 8.

$$T\Delta S^\circ = T\Delta S^\circ + \alpha\Delta H^\circ \dots\dots\dots 3$$

The plot shows a good correlation with  $R^2 = 0.9954$ . The intercept is 15.64 and 0.99 as slope. This suggests that the entropic change consists of two components. This first is independent of the enthalpy change ( $T\Delta S^\circ$ ) and the second is proportional to ( $\alpha\Delta H^\circ$ ), the proportionality factor might be considered as a quantitative measure of the enthalpy-entropy compensation. The positive intercept value indicated that the complexation is favored in the absence of an enthalpic contribution. This emphasizes that the complex formation is entropy favored while is enthalpy unfavored.

Previous studies showed enthalpy-entropy compensation effect. The complexes of thiacrown ether and calixcrown ethers with  $I_2$  showed enthalpy-entropy compensation with 0.8 correlation coefficient [18]. This was explained that the entropic change consists of two components, the first is independent of enthalpy change  $T\Delta S^\circ$  and the second is proportional to  $\alpha\Delta H^\circ$ . The enthalpy-entropy compensation was also investigated with  $K^+$  bis-crown ethers complex [19]. The results show the existence of this phenomena with  $\alpha = 1.03$  and intercept of 4.6 and correlation coefficient 0.99. Our results and these previously published are shown in Table 2 [19,20]. The slope  $\alpha$  is related to the degree of ligands conformational change and desolvation are involved upon complexation in each case and the intercept ( $T\Delta S^\circ$ ) to the extent of cations and ligand salvation. Thus the largest  $\alpha$  obtained for bis-crown ether reveals that this class of ligand experience substantial conformational change. The second largest intercept ( $T\Delta S^\circ$ ) also demonstrates that the cation accumulated in the cavity suffers extensive desolvation. Quantitatively, the unit slope  $\alpha = 1$  and the large intrinsic entropy gain ( $T\Delta S^\circ = 4.6$ ) jointly that the enthalpic gain arising from cation binding is completely canceled by the entropic loss from bis-crown ethers conformational change required upon complexation.

### Conclusion

The electron- donor macrocyclic compounds used in this study and the electron -acceptor fullerene  $C_{60}$  form charge transfer complexes with 1:1 stoichiometry. The obtained  $K_c$  values were dependent on many factors including cavity size, types of heteroatoms and substituents on the macrocycle. The thermodynamic study showed an enthalpy-entropy compensation effect.

Further studies on different macrocyclic compounds with  $C_{60}$  are under investigation to study thoroughly the factors which effect the complexation constant.

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