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Theoretical and Structural Relationship Study of Electrochemical Properties of *p*-Sulfonated Calix[8]arene Macrocycles with Fullerenes as [*p*-Sulfonated Calix[8]arenes]@[C_n] Supramalecular Complexes

Avat (Arman) Taherpour[1,*], Karim Zare[2,3], Leila Bakhtiari[1]

[1]Chemistry Department, Faculty of Science, Arak Branch, Islamic Azad University, P. O. Box 38135-567, Arak, Iran
[2]Chemistry Department, Science and Research Branch, Islamic Azad University, Tehran, Hesarak, Iran
[3]Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran

ABSTRACT

Up to now, various empty carbon fullerenes with different magic number "n", such as C_{20}, C_{60}, C_{70}, C_{80}, C_{180}, C_{240} and so on, have been obtained. The calix[n]arenes are a class of chalice-like macrocyclic molecules that have attracted widespread attention as complex molecules with liquid crystal behaviors. These classes of compounds are cyclic oligomers synthesized by condensation of a *para*-alkylated phenol and formaldehyde. Quantitative structural relationships have been successfully used to construct effective and useful mathematical methods for finding good relationships between structural data and the various chemical and physical properties. To establish a good structural relationship between the structures of fullerenes C_n (n = 60, 70, 76, 82 and 86) with *p*-sulfonated calix[8]arene as supramolecular [*p*-sulfonated calix[8]arene]@[C_n] complexes was utilized the number of carbon atoms of the fullerenes "n". In this study, the relationship between number of carbon atoms and the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) as assessed using oxidation reduction equation between fullerenes C_n (n = 60, 70, 76, 82 and 86) **1-5** and *p*-sulfonated calix[8]arene (**6**) as [*p*-sulfonated calix[8]arene]@[C_n] supramolecular complexes (A-E) are presented. The results were extended to calculate the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of other supramolecular complexes for fullerenes C_{60} to C_{300} and *p*-sulfonated calix [8] arenes **A-1** to **R-4**.

Keywords: Calix[8]arenes; Fullerenes; Free energy of electron transfer; Electrochemical properties

INTRODUCTION

Molecular guest-host systems have attracted enormous interest in recent years.[1-6] A guest molecule may also be more less permanently included in cage-type molecules of the carcerand or hemi-carcerand type [7-9] or reversibly encapsulated in hollow assemblies held together by electrostatic forces.[1,10,11,18] Calix[n]arenes are a class of macrocycles that have attracted much interest because of their potential for forming host-guest complexes and have been extensively investigated in various fields [12-24]. Calix[n]arenes with various functions have been developed with remarkable progress by modifying either the upper or lower rim [12-19, 25]. Especially, for developing calix[n]arenes as analytical reagents, upper or lower rim-modified calix[n]arenes have been applied for ion and molecular separations [17-20], as well as sensors such as ion and molecular selective electrodes and also liquid crystals [18-33]. Although all members of the series of calix[n]arenes (n = 4 to 20) have been known, even oligomers (tetramers, hexamers, octamers, etc.) are series to synthesize than odd ones [34]. Calixarenes can provide

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[*].Corresponding Author. avatarman.taherpour@gmail.com

insights into the binding of both electroinactive and electroactive guest species. These compounds can open up new avenues for immobilization of these receptor molecules onto surfaces[34a].

The water-soluble *p*-sulfonated sodium salt of calix[8]arene was synthesized before.[34a] The electrochemical behaviors and synthesis of *p*-sulfonated sodium salt calix[8]arenas **6** in NaAc+HAc (pH=4) buffer solution was studied and reported by Dian *et al.* in 2007[34a].

The unique stability of molecular allotropic forms such as C_{60} and C_{70} was demonstrated in 1985[35]. This event led to the discovery of a whole new set of carbon-based substances known as fullerenes.

After the discovery of C_{60} peapods by Luzzi *et a.* [35-37a], the aligned structure of encapsulated molecules due to the molecule-molecule and/or molecule-SWNT interactions has been studied as a new type of hybrid material [37b]. Zhang et al. [37c] reported evidence for the latter interaction by a measurement of the thermal stability of C_{60} peapods[37a-c].

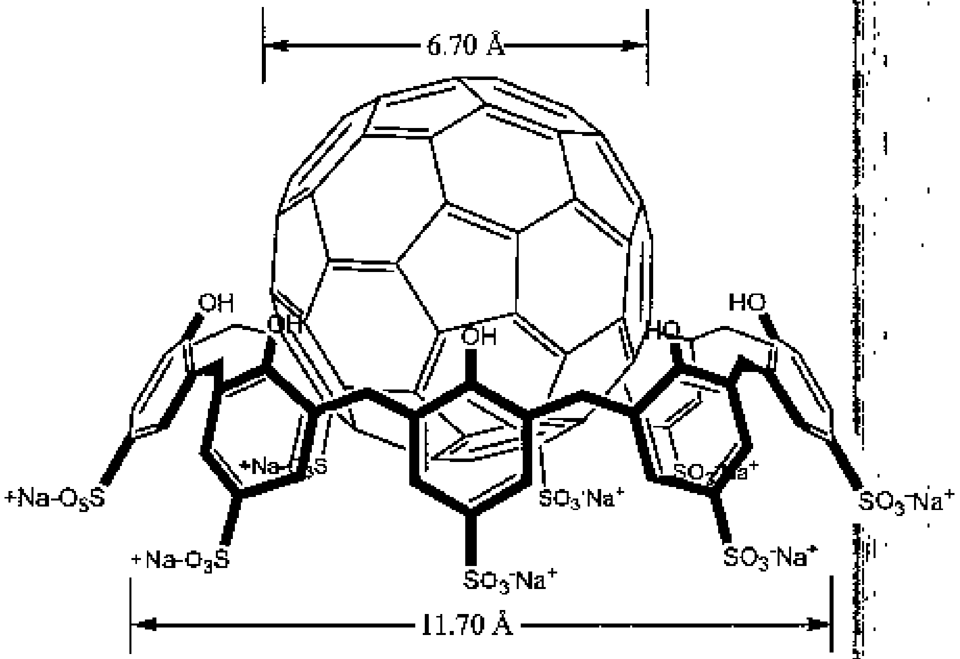

Fig.1. Imaginary supramolecular [*p*-sulfonated calix[8]arene]@[C_{60}] Complexes (**1** with **6**).

The electrochemical properties of the fullerene C_{60} have been studied since the early 1990s, when these materials became available in macroscopic quantities (for a review see [39])[36-39]. In 1990, Haufler *et al* [40]. have shown that C_{60} is electrochemically reducible in the CH_2Cl_2 medium to C_{60}^- and C_{60}^{2-}. In 1992, Echegoyen *et al.* [41] have cathodically reduced both C_{60} in six reversible one-electron steps for -0.97 vs. Fc/Fc$^+$ (Fc=ferrocene). This fact, along with the absence of anodic electrochemistry of fullerenes, matches the electronic structure of fullerenes: the LUMO of C_{60} can accept up to six electrons to form C_{60}^{6-}, but the position of the HOMO does not allow for hole-doping under the usual electrochemical conditions. In 1991, Bard *et al* [42]. first reported on irreversible electrochemical and structural reorganization of solid fullerenes in acetonitrile medium. Dunsch et al [43]. have upgraded the experimental conditions by investigating highly organized C_{60} films on HOPG in aqueous medium. The reduction of such films manifested itself by re-structuring into conductive nanoclusters of ~10^2 nm in diameter [43, 44]. The first reduction potentials of C_{60}, C_{70}, C_{76}, C_{82} and C_{86} were measured by T. Suzuki *et al.* in 1996 [45]. The first reported oxidation potentials are +1.21,

+1.19, +0.81, +0.72 and +0.73 Volt for C_{60}, C_{70}, C_{76}, C_{82} and C_{86}, respectively.

Graph theory has been found to be a useful tool in assessing the *QSAR* (Quantitative Structure Activity Relationship) and *QSPR* (Quantitative Structure Property Relationship)[46-54]. Numerous studies in the above areas have also used that are called topological indices (TI).[48-51] It is important to use effective mathematical methods to make good correlations between several data properties of chemicals. Numerous studies have been performed related to the above mentioned fields by using the so-called topological indices (TI) [46-54]. In 1993 and 1997, a related complex of applications of the Wiener and Harary indices in fullerene science was reported [51-54]. The numbers of carbon atoms at the structures of the fullerenes were utilized here.

In this study, the relationship between this index and the relationship between number of carbon atoms and the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) as assessed using the oxidation-reduction equation between **1-5** and *p*-sulfonated calix[8]arene (**6**) as [*p*-sulfonated calix[8]arene]@[C_n] supramolecular complexes (**A-E**) are presented. The results were extended to calculate the four free energies of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of other supramolecular complexes for fullerenes C_{60} to C_{300} and *p*-sulfonated calix[8]arenas **A-1** to **R-4**. By this model can predict a series of structures of [*p*-sulfonated calix[8]arene]@[C_n] complexes which they have made a good possibility to soluble and transfer fullerenes C_n in water or polar media as an emulsion.

GRAPHS AND MATHEMATICAL METHOD

All graphing operations were performed using the *Microsoft Office Excel 2003* program. The numbers of carbon atoms at the structures of the fullerenes C_n were utilized to make the relationship and calculate the first oxidation potentials ($^{ox}E_I$) of C_n fullerenes and the free energies of electron transfer ($\Delta G_{et(1)}$) as assessed using the Rehm-Weller equation for the supramolecular [*p*-sulfonated calix[8]arene]@[C_n] (**A-E**) complexes.

For modeling, both linear (MLR) and nonlinear (ANN) models were used in this study. To calculate the values that were not reported previously, equations 1-5 of this study were utilized. Some of the other indices were examined, and the best results and equations for extending the physicochemical data were chosen[46, 47, 52-54].

DISCUSSION

The structures of *p*-sulfonated calix[n]arenes (n = 4, 6, 8) and their electrochemical properties were reported by G.-W. Diao. [34a-c, 58, 59] Pailleret et al. [58, 59] reported the electrochemical characteristics of *p*-sulfonated calix[6]arene. The results showed that *p*-sulfonated calix[n]arene (n=4 and 6) could be oxidized at 0.7-0.8 Volt vs SCE. The studies have showed that it was easier to oxidize *p*-sulfonated calix[4]arene than *p*-sulfonated calix[6]arene. *p*-Sulfonated calix[8]arene **6** is similar to *p*-sulfonated calix[4]arene and *p*-sulfonated calix[6]arene, which can also be oxidized at a potential of 0.7-0.9 Volt vs SCE. [34a-d] *p*-Sulfonated calix[8]arene **6** was synthesized by the reactions of calyx[8]arene with concentrated H_2SO_4 [34a-d] The electrochemical properties of sodium salt of *p*-sulfonated calix[8]arene **6** in NaAc(0.5 M) +HAc(0.5 M) (pH=4) buffer solution was reported by G.-W. Diao et al. in 2007.[34a] In aqueous solution, *p*-sulfonated calix[8]arene can be oxidized when the potential is more than 0.7 Volt vs SCE. It was confirmed that the reaction was a two-electron irreversible electrochemical reaction. The anodic peak potential is 0.83V (vs SCE at 25°C and pH=4).[34a] The methyl ether of calix[8]arene crystallizes from $CDCl_3$ with two molecules of the solvent per molecule of host. An X-ray structural investigation has shown that the $CDCl_3$ guests exist within the calixarene framework. The complex resides on a crystallographic center of inversion, and the cavity is roughly circular in projection as measured by the distance between centroids of aromatic rings related by the center: 14.5, 13.9, 10.1, and 11.2 Å. Six of the oxygen atoms are found on the inside and two on the outside[55,56]. In contrast, the inner cavity diameters of calix[4]arene, calix[6]arene and calix[8]arene are 3.0, 7.6, and 11.7Å, respectively[56, 57]. The cavity size of *p*-sulfonated calix[8]arene **6** is more suitable than the smaller *p*-sulfonated calix[n]arenes to construction the structures of supramolecular [*p*-sulfonated calix[8]arenes]@[C_n] complexes. The diameter size of C_{60} was calculated to be 6.70Å [36, 47, 52]. The diameter size of fullerenes C_n (n =20, 24, 26, 36, 56, 58, 60, 70, 76, 78, 80, 82, 84, 120, 132, 140, 146, 150, 160, 162, 180, 240, 276, 288 and 300) were calculated and reported before.[36, 52]. The Reduction potentials (${}^{red}E_1$ to ${}^{red}E_4$) of fullerenes C_n (*n*=60, 70, 76, 82 and 86) were reported [45]. Four reported reduction potentials (${}^{Red}E_1$ to ${}^{Red}E_4$) of fullerenes C_n for: C_{60} are, -1.12, -1.50, -1.95 and -2.41V, respectively.[45] The data of ${}^{Red}E_n$(Volt, n=1-4) for C_{70} are: -1.09, -1.48, -1.87 and -2.30V, respectively.[45] The values of ${}^{Red}E_n$(Volt, n=1-4) for C_{76} are: -0.94, -1.26, -1.72 and -2.13V, respectively.[45] Four values of ${}^{Red}E_n$(Volt, n=1-4) for C_{82} are: -0.69, -1.04, -1.58 and -1.94V, respectively.[45] The amounts of ${}^{Red}E_n$(Volt, n=1-4) for C_{86} are: -0.58, -0.85, -1.60 and -1.96V, respectively.[45] See Table 1. The twenty calculated values of the four electron transfer free energies ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) in kcal mol^{-1} between *p*-sulfonated calix[8]arene **6** and C_n as [*p*-sulfonated calix[8]arene]@[C_n] complexes (n = 60, 70, 76, 82 and 86), by utilize oxidation-reduction equation (Eq.-1) were shown in Table 1.

The relationship between the number of carbon atoms of fullerenes "n" and the first, second, third and fourth free energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) of [*p*-sulfonated calix[8]arene]@[C_n] complexes (n = 60, 70, 76, 82 and 86) are demonstrated in Fig.-2 to Fig.-5. Equations 2 to 5 are related to Fig.-2 to Fig.-5. They are second-order polynomial equations. The R-squared values (R^2) for these graphs are: 0.9875, 0.9923, 0.9384 and 0.9473, respectively.

$$\Delta G_{et(1)} = -0.0235(n)^2 + 2.9201(n) - 46.240 \quad \text{(Eq.-2)}$$

$$\Delta G_{et(2)} = -0.0280(n)^2 + 3.4983(n) - 55.733 \quad \text{(Eq.-3)}$$

$$\Delta G_{et(3)} = -0.0025(n)^2 + 0.0125(n) + 72.031 \quad \text{(Eq.-4)}$$

$$\Delta G_{et(4)} = -0.0039(n)^2 + 0.1108(n) + 81.570 \quad \text{(Eq.-5)}$$

By the use of equations 1-5, it is possible to calculate the values of $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of [*p*-sulfonated calix[8]arene]@[C_n] complexes (n = 60, 70, 76, 82 and 86). The twenty calculated values **A-1** to **E-4** of the four free energies of electron transfer ($\Delta G_{et(n)}$, n=1-4) in kcal mol^{-1} between [*p*-sulfonated calix[8]arene] **6** complexes, were shown in Table-1. The data of $\Delta G_{et(n)}$ (n=1-4) for [*p*-sulfonated calix[8]arene]@[C_n] (n= C_{60}, C_{76}, C_{76}, C_{62}, C_{86}, C_{78}, C_{84}, C_{120}, C_{132}, C_{146}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{276}, C_{288} and C_{300}) C_{60} **(A-1** to **A-4)**, C_{76} **(B-1** to **B-4)**, C_{76} **(C-1** to **C-4)**, C_{62} **(D-1** to **D-4)**, C_{66} **(E-1** to **E-4)**, C_{78} **(F-1** to **F-4)**, C_{84} **(G-1** to **G-4)**, C_{120} **(H-1** to **H-4)**, C_{132} **(I-1** to **I-4)**, C_{140} **(J-1** to **J-4)**, C_{146} **(K-1** to **K-4)**, C_{150} **(L-1** to **L-4)**, C_{160} **(M-1** to **M-4)**, C_{162} **(N-1** to **N-4)**, C_{240} **(O-1** to **O-4)**, C_{276} **(P-1** to **P-4)**, C_{288} **(Q-1** to **Q-4)**, C_{300} **(R-1** to **R-4)**) are predicted by using Eq.-2 to Eq.-5 and the oxidation-reduction equation. See Table-2. The calculated values of the free electron transfer of $\Delta G_{et(n)}$ **(n=1-4)** for [*p*-sulfonated calix[8]arene]@[C_n] (n = 60, 70, 76, 82 and 86, **A-1** to **E-4**) were reported by oxidation-reduction equation and Eq.-2 to Eq.-5 and compared in Table-2. There were good coherencies between the calculated and the predicted values. In lieu of increasing the number of carbons at the structures of fullerenes, the values of $\Delta G_{et(n)}$ (n=1-4) decreased. It seems that the electron transfers getting increase by increasing the electron population at the C_n structures. Table-1 shows that the four reduction potentials (${}^{Red}E_1$ to ${}^{Red}E_4$) increased by increasing the number of carbon atoms at the fullerenes. These results may return back to HOMO and LUMO gap of the fullerenes. The calculated values of the free energy of electron transfer of $\Delta G_{et(n)}$ (n=1-4) for [*p*-sulfonated calix[8]arene]@[C_n] were decreased by increasing the number of carbon atoms and size of the fullerenes. It seems that in each of the series of the four free energy of electron transfer were diminished (because of the limited cavity size of [*p*-sulfonated calix[8]arene]) by the increasing the distances between two parts of these complexes (i.e: [*p*-sulfonated calix[8]arene] and C_n) and increasing the dimensions of the fullerenes. Table-2 has showed that all of the free electron transfer $\Delta G_{et(n)}$ (n=1-4) values of [*p*-sulfonated calix[8]arene]@[C_{60}] **A-1** to [*p*-sulfonated calix[8]arene]@[C_{300}] **R-4** are minus. The structures of the supramolecular complexes which were discussed here, the calculated values of $\Delta G_{et(n)}$ (n=1-4) concern to these supramolecular complexes were neither synthesized nor reported before.

Table1. The values of the four reported reduction potentials ($^{Red}E_1$ to $^{Red}E_4$, Ref.[45]) of fullerenes C_n (n = 60, 70, 76, 82 and 86) and the values of the free energy of electron transfer (ΔG_{et}) in kcal mol^{-1} of the upramolecular of [*p*-Sulfonated Calix[8]arenes]@[C_n]supramolecular complexes (A-E) complexes by oxidatian-reduction equation

Id	[*p*-sulfonated calix[8]arenes]@[C_n]*	$^{Red}E_1$	$\Delta G_{et(1)}$*	$^{Red}E_2$	$\Delta G_{et(2)}$*	$^{Red}E_3$	$\Delta G_{et(3)}$*	$^{Red}E_4$	$\Delta G_{et(4)}$*
		1		2		3		4	
A	[*p*-SCA]@C_{60}	-1.12	44.27	-1.50	53.04	-1.95	63.41	-2.41	74.02
B	[*p*-SCA]@C_{70}	-1.09	43.58	-1.48	52.58	-1.87	61.57	-2.30	71.49
C	[*p*-SCA]@C_{76}	-0.94	40.12	-1.26	47.50	-1.72	58.11	-2.13	67.57
D	[*p*-SCA]@C_{82}	-0.69	34.36	-1.04	42.43	-1.58	54.88	-1.94	63.18
E	[*p*-SCA]@C_{86}	-0.58	31.82	-0.85	30.05	-1.60	55.34	-1.96	63.65

* The data of the free energy of electron transfer (ΔG_{et}) for the compounds and their complexes were nat reported, previously. The compounds [*p*-Sulfonated Calix[8]arenes]@[C_n] supramolecular complexes (A-E) were neither synthesized nor reported.

Table 2. The values of the free energy of electron transfer (ΔG_{et}) in kcal mol^{-1} of [*p*-Sulfonated Calix[8]arenes]@[C_n]supramolecular complexes(A-R) supramolecular complexes. The data of ($\Delta G_{et(n)}$) (Volt, n=1-4) for **A-1** to **Q-4** by using Eq.-2 to Eq.-5 and the oxidation-reduction equation

Id.	[*p*-Sulfonated Calix[8]arenes]@[C_n]*	$\Delta G_{et(1)}$* 1	$\Delta G_{et(2)}$* 2	$\Delta G_{et(3)}$* 3	$\Delta G_{et(4)}$* 4
A	[*p*-SCA]@C_{60}	44.27 (44.37)	53.04 (53.37)	63.41 (63.78)	74.02 (74.18)
B	[*p*-SCA]@C_{70}	43.58 (43.02)	52.58 (51.95)	61.57 (60.65)	71.49 (70.22)
C	[*p*-SCA]@C_{76}	40.12 (39.95)	47.50 (48.41)	58.11 (58.54)	67.57 (67.46)
D	[*p*-SCA]@C_{82}	34.36 (35.20)	42.43 (42.86)	54.88 (56.24)	63.18 (64.44)
E	[*p*-SCA]@C_{86}	31.82 (31.08)	38.05 (38.03)	55.34 (54.61)	63.65 (62.26)
F	[*p*-SCA]@C_{78}	38.56	46.79	57.79	66.48
G	[*p*-SCA]@C_{84}	33.23	4056	55.44	63.36
H	[*p*-SCA]@C_{120}	-34.23	-39.13	37.53	38.71
I	[*p*-SCA]@C_{132}	-70.25	-81.82	30.12	28.25
J	[*p*-SCA]@C_{140}	-98.03	-114.77	24.78	20.64
K	[*p*-SCA]@C_{146}	-120.84	-141.83	20.56	14.62
L	[*p*-SCA]@C_{150}	-136.98	-160.99	17.65	10.44
M	[*p*-SCA]@C_{160}	-180.62	-212.80	10.03	-0.54
N	[*p*-SCA]@C_{162}	-189.91	-223.84	8.45	-2.83
O	[*p*-SCA]@C_{240}	-699.02	-828.94	-68.97	-116.48
P	[*p*-SCA]@C_{276}	-1030.43	-1223.13	-114.96	-184.94
Q	[*p*-SCA]@C_{288}	-1154.43	-1370.65	-131.73	-210.00
R	[*p*-SCA]@C_{300}	-1285.21	-1526.24	-149.22	-236.19

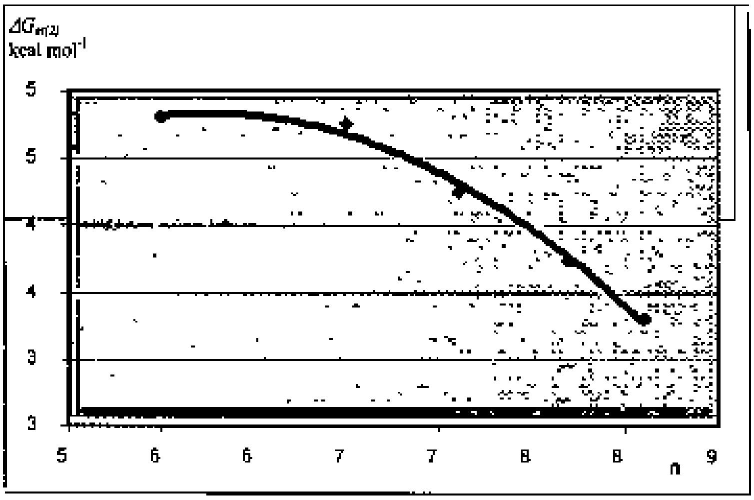

Fig.2. The curve of the relationship between the number of carbon atoms of fullerenes "n" and the first free energy of electron transfer ($\Delta G_{et(1)}$) of [*p*-Sulfonated Calix[8]arenes]@[C_n] (n = 60, 70, 76, 82 and 86), compounds **A** to **E**.

*The data of the free energy of electron transfer ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) for [*p*-Sulfonated Calix[8]arenes]@[C_n]supramolecular complexes (**A-R**) were not reported, previously.

**The results in parentheses concern to the results of the oxidation-reduction equation.

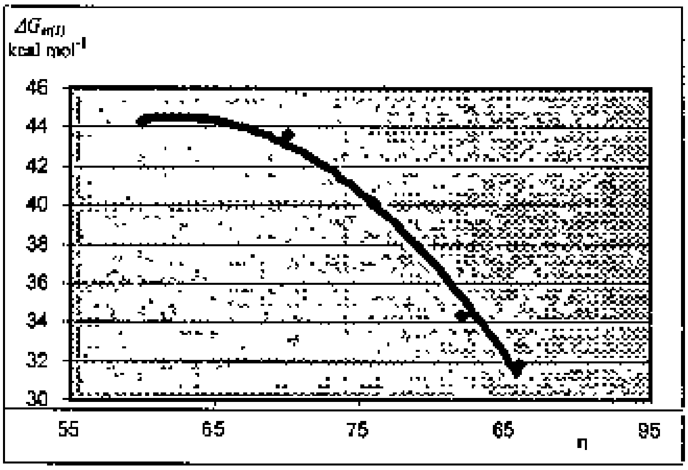

Fig.3. The curve of the relationship between the number of carbon atoms of fullerenes "n" and the second free energy of electron transfer ($\Delta G_{et(2)}$) of [*p*-Sulfonated Calix[8]arenes]@[C_n] (n = 60, 70, 76, 82 and 86), compounds **A** to **E**.

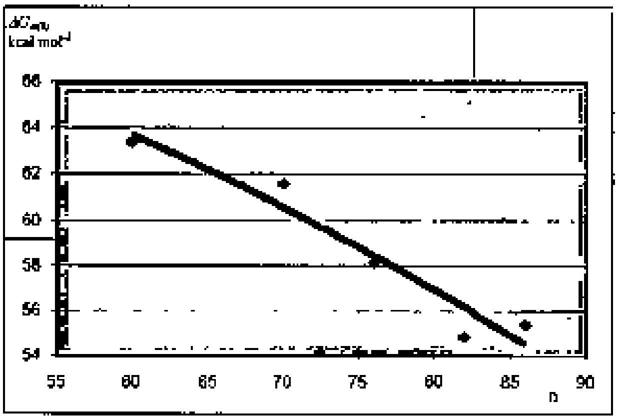

Fig.4. The curve of the relationship between the number of carbon atoms of fullerenes "n" and the third free energy of electron transfer ($\Delta G_{et(3)}$) of [*p*-Sulfonated Calix[8]arenes]@[C_n] (n = 60, 70, 76, 82 and 86), compounds **A** to **E**.

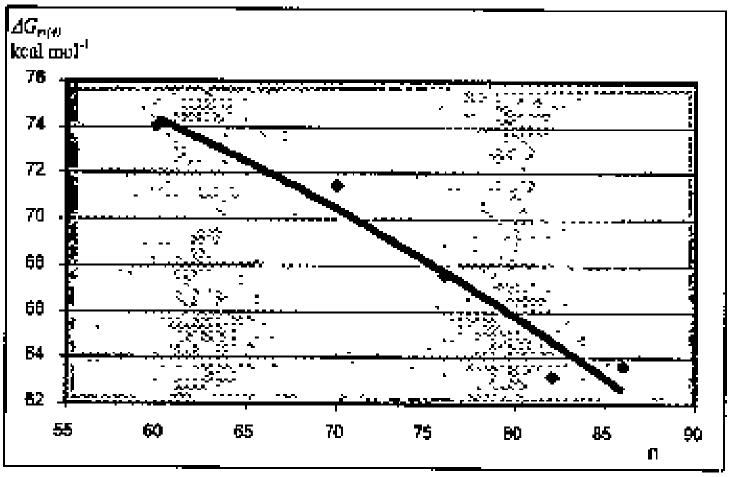

Fig.5. The curve of the relationship between the number of carbon atoms of fullerenes "n" and the fourth free energy of electron transfer ($\Delta G_{et(4)}$) of [p-Sulfonated Calix[8]arenes]@[C_n] (n = 60, 70, 76, 82 and 86), compounds A to E.

CONCLUSION

The p-sulfonated calix[n]arenes and fullerenes have important physicochemical properties. The four free energy of electron transfer data of [p-sulfonated calix[8]arene]@[C_n] (n = 60, 70, 76, 82 and 86, A-1 to E-4) were calculated here ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) as assessed using the oxidation-reduction equation. The 72 calculated values of ($\Delta G_{et(1)}$ to $\Delta G_{et(4)}$) for A-1 to R-4 were calculated by using the oxidation-reduction equation. Using the number of carbon atoms (n) to the product the equations of the model can derive sound structural relationships between the aforementioned physicochemical data. By utilizing the equations of this model, can calculate in good approximation the $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ for [p-sulfonated calix[8]arene]@[C_n] (n= C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}, C_{84}, C_{120}, C_{132}, C_{140}, C_{146}, C_{150}, C_{160}, C_{162}, C_{240}, C_{270}, C_{288} and C_{300}) C_{60} (**A-1** to **A-4**), C_{70} (**B-1** to **B-4**), C_{76} (**C-1** to **C-4**), C_{82} (**D-1** to **D-4**), C_{86} (**E-1** to **E-4**), C_{78} (**F-1** to **F-4**), C_{84} (**G-1** to **G-4**), C_{120} (**H-1** to **H-4**), C_{132} (**I-1** to **I-4**), C_{140} (**J-1** to **J-4**), C_{146} (**K-1** to **K-4**), C_{150} (**L-1** to **L-4**), C_{160} (**M-1** to **M-4**), C_{162} (**N-1** to **N-4**), C_{240} (**O-1** to **O-4**), C_{270} (**P-1** to **P-4**), C_{288} (**Q-1** to **Q-4**), C_{300} (**R-1** to **R-4**)). This model predicted that the [p-sulfonated calix[8]arene]@[C_n] molecules are suitable to make emulsion systems for fullerenes. The supramolecular complexes and $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ where discussed here were previously neither synthesized nor reported.

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