9064 *J. Phys. Chem. A* **2004,** *108,* 9064−9068

Study of Host−Guest Interaction of [70]Fullerene with Substituted Calix[6]arenes by Absorption Spectrometric Method

Sumanta Bhattacharya,*,† Sandip K. Nayak,‡ Abha Semwal,‡ Subrata Chattopadhyay,‡ and Manas Banerjee†

Department of Chemistry, The University of Burdwan, Golapbag, Burdwan - 713 104, India, and Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai - 400 085, India

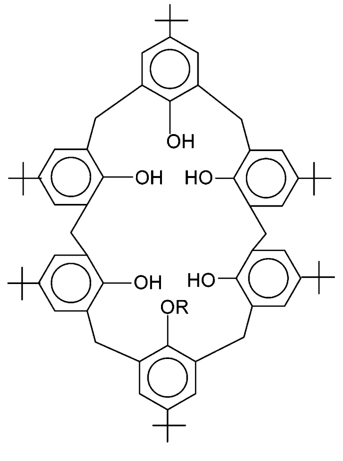
Received: May 2, 2004; In Final Form: July 31, 2004

The host−guest interaction of various mono O-substituted calix[6]arenes, namely, (i) 37-benzyl-38,39,40,41,42-pentahydroxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**1**), (ii) 37-ethylester-38,39,40,41,42-pentahydroxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**2**), and (iii) 37-allyl-38,39,40,41,42-pentahydroxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**3**) with [70]fullerene has been studied in a CCl_4 medium by the absorption spectroscopic method. All of the complexes are found to be stable with 1:1 stoichiometry. An absorption band due to a charge transfer (CT) transition is observed in the visible region; with increasing ionization potential of the mono O-substituted calix[6]arenes, the peak energy shifts to the higher energy side and the oscillator strength of CT transition increases. Degrees of CT have been estimated by analyzing the CT transition energy as a function of ionization potential. Thermodynamic parameters for the supramolecular complex formation of [70]fullerene with **1**, **2**, and **3** receptors are reported. The high formation constant value for the [70]fullerene·**2** complex indicates that **2** forms an inclusion complex with [70]fullerene.

1. Introduction

After its discovery in 1984,[1] the new form of carbon, namely [70]fullerene, has generated an avalanche of research activity.[2,3] The interest in such a novel material has especially increased because of its versatile application in superconductivity,[4] ferromagnetism,[5] and biological activity.[6] The appreciable electron affinity of [70]fullerene[7] makes it an efficient electron acceptor, and the study of the formation of electron donor−acceptor (EDA) complexes of [70]fullerene in both the ground and excited strates is finding increasing attention day by day.[8−15]

The complexation between calix[*n*]arenes[16−19] and fullerenes[1] has evoked a new dimension in supramolecular chemistry. Calix[*n*]arenes not only have well-ordered macrocyclic arrays of aromatic rings but also possess the necessary flexibility to allow docking of large guest molecules, such as fullerenes. This expectation has become a reality when selective formation of clathrate from [60]fullerene and calix[8]arene was extensively utilized for the separation of [60]- and [70]fullerenes.[20,21] Construction of supramolecualr architectures involving electron-deficient fullerene is of current interest in crystal engineering and the synthesis of novel nanostructures.[22,23] Molecules of large ring size and deep cavity are of interest in host−guest chemistry, and inclusion studies involving the binding of large molecules and ions are being conducted. Mono O-substituted calix[6]arenes represent a family of such host molecules, for which, in principle, efficient inclusion could occur, because multiple $\pi-\pi$ interactions between the guest and host are possible. But, for mono O-substituted calix[6]arenes, inclusion studies are very limited. Through this study, it has been established that, with the help of a smooth and electron-dense surface, [70]fullerene can be bound to the host calix[6]arene with a suitable cavity size whereby [70]fullerene can reside endo and exo relative to the cavity of the calix[6]arenes, and this will modulate the $\pi-\pi$ interactions and spatial interplay of the [70]fullerene. Thus, the nature of substitution on the lower rim of the calix[6]arenes plays a very significant role during host−guest complexation with [70]fullerene.



1 : R = benzyl (-CH_2Ph)

2: R = ethyl ester (-CH_2-CO_2Et)

3 : R = allyl (-CH_2-$CH{=}CH_2$)

Figure 1. Structure of the calix[6]arenes studied.

2. Materials and Methods

[70]Fullerene was obtained from SES Research Corporation, Texas. The substituted calix[6]arenes (Figure 1) were prepared according to the method in ref 24, and their purity was checked

---

* Corresponding author. E-mail: sum_9974@rediffmail.com.

† The University of Burdwan.

‡ Bhabha Atomic Research Centre.

10.1021/jp0481106 CCC: $27.50

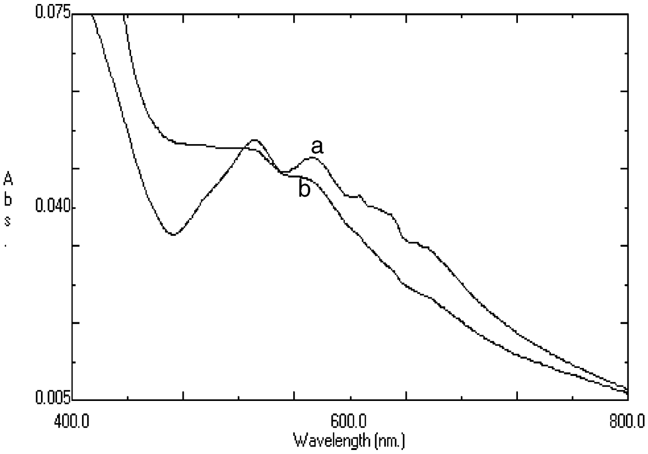


Figure 2. CT absorption spectra of (a) [70]fullerene + **2** and (b) [70]fullerene + **3** against pristine acceptor solution as reference.

TABLE 1: Gaussian Curve Analysis for the CT Spectrum of [70]Fullerene with 1, 2, and 3

system	area of the curve (A)	width of the curve (w)	center of the curve (x_c)	y_0
[70]fullerene·**1**	1.64 ± 3.46	63. 6 ± 51.4	486 ± 0.9	0.18 ± 0.03
[70]fullerene·**2**	2.08 ± 1.10	82.2 ± 18.2	640 ± 1.7	0.014 ± 0.01
[70]fullerene·**3**	0.22 ± 0.18	32.6 ± 12.2	561 ± 1.2	0.04 ± 0.002

by NMR spectra of the purified samples. The solvent CCl_4 was purified by drying over fused $CaCl_2$, followed by distillation. Spectral measurements were done on a Shimadzu UV - 1601 PC model spectrophotometer fitted with a Peltier controlled thermobath.

3. Results and Discussion

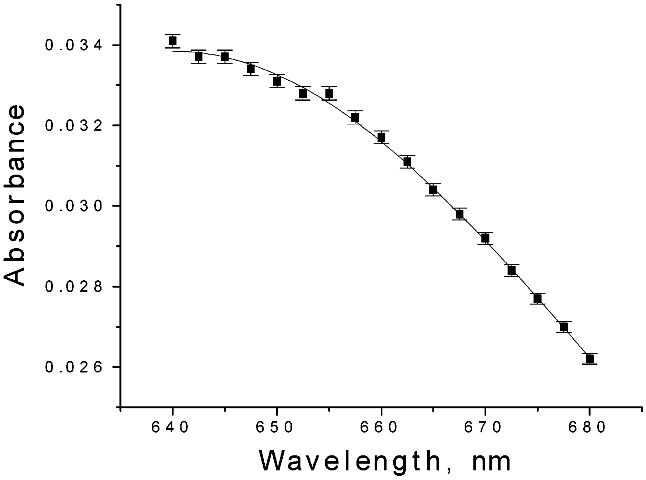


Figure 3. Gaussian analysis curve of the shoulder region of Figure 2a.

TABLE 2: CT Absorption Maxima and Transition Energies of [70]Fullerene Complexes; PM3-Determined IPs of the Calix[6]arenes; Degrees of CT (α), Oscillator Strength (*f*), and Transition Dipole Strength (μ_{EN}) of the Complexes of [70]Fullerene with 1, 2, and 3

calix[6]arene	λ_{CT}, nm	$h\nu_{CT}$, eV	PM3 I_D^v, eV	$10^2\ \alpha$	$10^4 \times f$	μ_{EN} (Debye)
1	486	2.55	8.687	3.70	10.9	6.0
2	640	1.94	8.677	3.71	1.7	3.4
3	561	2.21	8.671	3.72	8.9	7.6

3.1. Observation of CT Bands. Figure 2 shows the electronic absorption spectra of mixtures containing [70]fullerene with **2** and **3** in CCl_4 medium. All spectra of mixtures containing [70]fullerene and calix[6]arenes were recorded against the pristine acceptor solution as a reference to cancel out the [70]fullerene absorbance. It is observed that new absorption peaks appear in the visible region. The solvent CCl_4 and the calix[6]arenes (**2** and **3**) do not absorb in the visible region. The presently determined $h\nu$ values corroborate well with the third parametric method (PM3)-determined ionization potentials of the calix[6]arenes in accordance with Mulliken's equation.[25,26] The following type of equation was obtained with the present data

$$2I_D^v - h\nu_{CT} = (0.115 \pm 0.001)I_D^v(I_D^v - h\nu_{CT}) + (8.70 \pm 0.035) \quad (1)$$

with a correlation coefficient of 0.99. Thus, the transition energy ($h\nu$) can be termed as CT transition energy ($h\nu_{CT}$). It is a common experience that, in order to detect CT absorption bands in solution, the donor (in the present case, calix[6]arenes) concentration must be very high compared to that of the acceptor. For this reason, in a recent study on the complexation of calix[4]naphthalenes with [60]fullerene,[27] no CT band was reported. The reason is that the concentration of calix[4]naphthalenes was 10^{-4} mol·dm^{-3}, but in the present case, the mixture is ~10^{-2}−10^{-3} mol·dm^{-3} with respect to the calix[6]arenes in each case. The CT absorption spectra were analyzed by fitting to the Gaussian function

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} \exp \frac{-2(x - x_c)^2}{w^2}$$

where x and y denote wavelength and absorbance, respectively. The results of the Gaussian analysis for all of the calix[6]arenes under study are shown in Table 1. One important point to mention here is that Gaussian analysis of a curve generally gives a decent result near the maxima of the curve spread over a very small region. For this reason, although the errors in the center of the CT spectra for the complexes of [70]fullerene with calix[6]arenes are very small, there are appreciable errors in the curve area and width of the CT absorption spectra. One typical Gaussian analysis plot is shown in Figure 3. The wavelengths of the CT absorption maxima ($\lambda_{max} = x_c$) and the corresponding CT transition energies ($h\nu_{CT}$) are summarized in Table 2.

3.2. Degree of Charge Transfer (α). To discuss the degrees of charge transfer (α) for the [70]fullerene−calix[6]arene CT complexes, we have to take into account Mulliken's two-state model.[25] In this model, α is expressed[25,28] by

$$\alpha = \frac{\left(\frac{C_2}{2}\right)}{\left[\{(I_D^v - E_A^v + C_1)^2\} + \frac{C_2}{2}\right]} \quad (2)$$

The value of α is calculated by using eq 2 and given in Table 2. The low value of α indicates that very little charge transfer takes place in the ground state. The dependence of α on the I_D^v value of the donors is shown in Figure 4. It is found that α decreases with increasing ionization potential of the donors, as expected. Li et al.[29] have evaluated α = 0.57 for [60]fullerene−aniline complex by a theoretical method. They have calculated

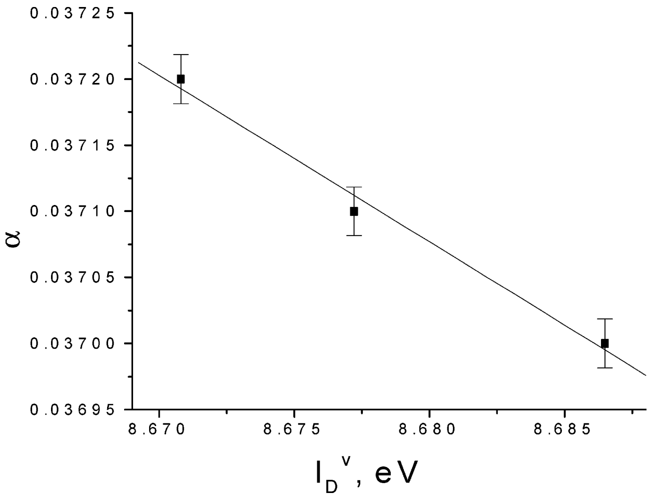


Figure 4. Degrees of charge transfer (α) as a function of ionization potential.

the charge distribution by the INDO method using the CT complex configuration that an aniline molecule resides perpendicularly on the surface of [60]fullerene and the amine group resides at the nearest position from [60]fullerene. The calculated α value is much larger than our present experimental one, which suggests that the CT complex configuration used in the calculation is inconsistent with our experimental results.

3.3. Determination of Oscillator Strength (*f*) and Transition Dipole Strength (μ_{EN}). From the CT absorption spectra, we can extract an oscillator strength.[30] The oscillator strength *f* is estimated using the following formula

$$f = 4.32 \times 10^{-9} \int \epsilon_{CT}\, d\nu \qquad (3)$$

where $\int \epsilon_{CT}\, d\nu$ is the area under the curve of the extinction coefficient of the absorption band in question vs frequency. To a first approximation calculated as follows

$$f = 4.32 \times 10^{-9}\, \epsilon_{max}\, \Delta\nu_{1/2} \qquad (4)$$

where ϵ_{max} is the maximum extinction coefficient of the band and $\Delta\nu_{1/2}$ is the half-width (i.e., the width of the band at half of the maximum extinction). The observed oscillator strengths of the CT bands are summarized in Table 2. It is worth mentioning that we need a proper calculation of oscillator strength of [70]fullerene−calix[6]arene CT complexes. This is because oscillator strength is very sensitive to the molecular configuration and the electron charge distribution in the CT complex. In the [70]fullerene−calix[6]arene complexes, we cannot use a simple model assuming a charge localized at a certain site of a fullerene sphere; this is because fullerenes have π-bonds which are directed radially with a node on the molecular cage.

The extinction coefficient is related to the transition dipole[30] by

$$\mu_{EN} = 0.0952 \left(\frac{\epsilon_{max}\Delta\nu_{1/2}}{\Delta\nu}\right)^{1/2} \qquad (5)$$

where $\Delta\nu \approx \acute{\nu}$ at ϵ_{max} and μ_{EN} is defined as $-e \int \psi_{ex} \sum_i r_i \psi_g\, d\tau$. The μ_{EN} values for the [70]fullerene−calix[6]arene complexes are given in Table 2.

3.4. Determination of Formation Constant (*K*). The formation constants of the [70]fullerene−calix[6]arene complexes were determined at four different temperatures using the Benesi−Hildebrand (BH)[31] equation for a cell with a 1-cm optical path length in the following form:

TABLE 3: Data for Spectrophotometric Determination of Stoichiometry, Formation Constants (*K*'s), and Corrected Molar Absorptivities (ϵ''s) of the [70]Fullerene·1 Complex

temp (K)	10^3 donor concn (mol·dm^{-3})	10^5 $[A]_0$ (mol·dm^{-3})	corrected absorbance at 472 nm	*K* (dm^3·mol^{-1})	10^{-3} ϵ' (dm^3·mol^{-1}·cm^{-1})
298	0.30	1.853	0.041	1350 ± 65	8 ± 1
	0.42		0.051		
	0.53		0.068		
	0.70		0.069		
	0.81		0.068		
	0.95		0.078		
	1.04		0.093		
	1.18		0.088		
303	0.30		0.037	1150 ± 60	
	0.42		0.048		
	0.53		0.063		
	0.70		0.066		
	0.81		0.065		
	0.95		0.074		
	1.04		0.094		
	1.18		0.083		
308	0.30		0.029	750 ± 40	
	0.42		0.044		
	0.53		0.060		
	0.70		0.062		
	0.95		0.060		
	1.04		0.072		
	1.18		0.086		
			0.080		
313	0.30		0.026	550 ± 30	
	0.42		0.039		
	0.70		0.059		
	0.81		0.055		
	0.95		0.056		
	1.04		0.085		

$$\frac{[A]_0[B]_0}{d'} = \frac{[B]_0}{\epsilon'} + \frac{1}{K\epsilon'} \qquad (6)$$

Here, $[A]_0$ and $[B]_0$ are the initial concentrations of [70]fullerene and calix[6]arene, respectively, before complexation, d' is the corrected absorbance of the donor−acceptor mixture at the center (472 nm) of the perturbed broad peak of [70]fullerene resulting from forbidden singlet−singlet transitions[32,33] measured against the solvent as reference. The quantity ϵ' is the corrected molar absorptivity of the complex at the wavelength (472 nm) of measurement. *K* is the formation constant of the complex. The equilibrium constant values are calculated using the BH model, which is only an approximation. Sibley et al.[26] have also estimated the formation constants for the complexes of [60]fullerene with aniline and substituted anilines using the BH[31] equation. Absorbance data for one such system are shown in Table 3. The concentration data are given to only two significant figures (in most cases), and the absorption difference is given to two significant figures and is small, always less than 0.10. In all cases, very good linear plots according to eq 6 were obtained, one such plot being shown in Figure 5. Among all of the [70]fullerene−calix[6]arene complexes under study, *K* values of only one complex (viz., [70]fullerene·**2**) is indicative of the inclusion of [70]fullerene within the calix[6]arene cavity. The main perturbing factor present in **2** with respect to other two calix[6]arenes (e.g., **1** and **3** case) is the replacement of the H atom by an ethyl ester group, conferring a greater flexibility to

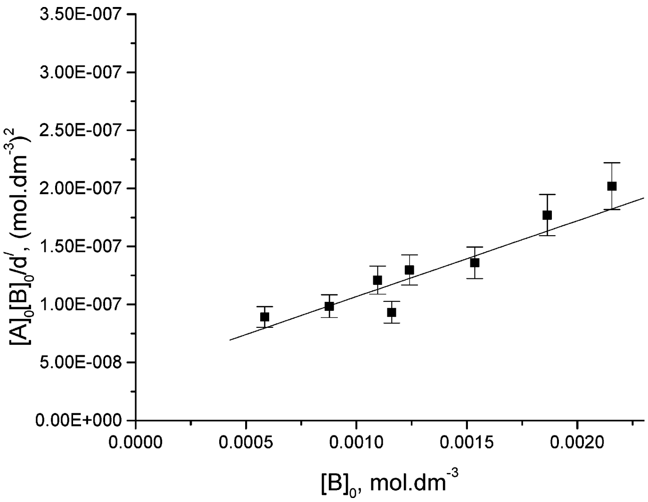


Figure 5. Benesi−Hildebrand plot for the complex of [70]fullerene with **2** at 303 K.

the molecule. The resulting conformation is analogous to the 1,2,3-alternate conformation in the calix[6]arenes. Inclusion of [70]fullerene is preceded by a preorganization of the calix[6]arene molecule into a conical conformation through intramolecular H-bonding at the lower rim. The self-inclusion of one methoxy substituent in a calix[4]arene derivative has been shown to have a significant effect on the conformer energy.[34] This is also the case in the present compound. Although the origin of this self-inclusion is unknown, the hypothesis can be made that dipole−dipole interactions between the two head-to-tail ester groups with hydroxy groups on the opposite ends, with a minimum separation, could play some role. The allyl and benzyl groups hinder the attainment of such a conical conformation. The allyl group attached to one oxygen atom hinders the attainment of cone conformation probably by a different mechanism: to extend π-conjugation via a lone pair of electrons of oxygen into the corresponding benzene ring of the calix[6]arene molecule, the allyl group turns the ring around, making it out-of-plane with respect to the other benzene rings of the calix[6]arene. This explains the observed order in the K values.

3.5. Enthalpies (ΔH_f^0) and Entropies of Formation (ΔS_f^0) of the Complexes of [70]Fullerene with Calix[6]arenes. In comparison with the large amount of data which has published on equilibrium constants of [60]fullerene−calix[n]arene complexes, relatively few attempts have been made to estimate enthalpies (ΔH_f^0) and entropies of formation (ΔS_f^0) for the complexes of [70]fullerene with calix[n]arenes. For example, Ikeda et al.[35] have measured the ΔH_f^0 values and compared them with values obtained from association constants estimated by spectroscopic method. In another study, Shinkai et al.[36] have measured the thermodynamic parameters for the complexes of calix[n]arenes with [60]fullerene in an organic solvent. As measured, these terms will represent the net change in enthalpy and entropy for the solvated species. Plots of ln K vs 1/T at four different temperatures for [70]fullerene with **1**, **2**, and **3** are linear and have positive slopes, indicating that the complexation process is exothermic and thus driven by favorable enthalpy changes. A typical plot of [70]fullerene and **1** in CCl_4, for example, gives a straight line ($r^2 = 0.98$) with a slope of 5.81×10^3 and an intercept of −12 (Figure 6). Similar results have been obtained in all of the cases studied. All of the ΔH_f^0 values determined for [70]fullerene−calix[6]arene complexes were exothermic and are listed in Table 4. The ΔH_f^0 values for the complexes of [70]fullerene with **1**, **2**, and **3** are higher than those obtained for the same solvent with *p-tert*-butyl calix[4]arenes and *p-tert*-butyl calix[6]arenes in some of our very recent work.[37] Presumably, the replacement of one H atom of the −OH group at the lower rim confers greater flexibility to the calix[6]arene molecules, which is very favorable for complexation with [70]fullerene. Also, additional attractive $\pi-\pi$ interactions are taking place in our present case. This additional $\pi-\pi$ interaction is due to the fact that the presence of substituent groups at the lower rim of calix[6]arene molecules results in the formation of a deeper and wider cavity, thus potentially allowing for better contact between host and guest.[38] Table 4 also shows that all of the ΔS_f^0 values are negative, indicating that, while complex formation is enthalpy-favored, it is also entropy-disfavored. Formation of the complexes therefore results in a more-ordered system, possibly due to freezing of the motional freedom of both the guest and host molecules. Tao and Barra have offered a similar rationale for the data they have observed with their particular system.[39] The higher ΔH_f^0 values observed for [70]fullerene·**1** and [70]fullerene·**3** systems, as compared to [70]fullerene·**2**, can be rationalized as follows: It has been suggested that a factor which could possibly contribute to the unusual binding trends observed may be desolvation of the [70]fullerene occurring to a lesser degree with calix[6]arene **2**. The entropy changes observed for the complexation of [70]fullerene with **1** and **3** are larger than that observed for **2**. It is due to the fact that a higher degree of residual solvation could provide some explanation for the smaller entropy loss and, hence, the stronger binding with the less-tight complex with the *p-tert*-butyl host **2**. In our present investigations, there are large errors in the entropy values in Table 4 as compared to the enthalpy values. This is because, between enthalpy and entropy, the former function is nearly independent of the particular solvent, providing that it is not a strongly solvating solvent. Finally, it can be concluded that, because the guest molecule (i.e., [70]fullerene) is a weak electron acceptor, CT interaction may also play an important role in complexation.

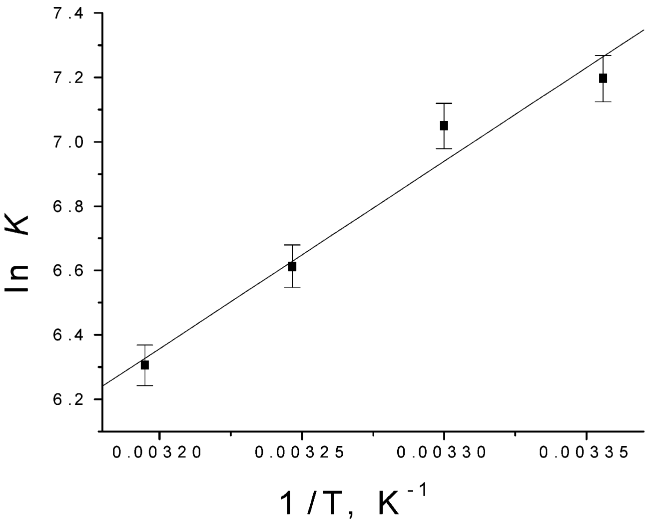


Figure 6. Plot for determination of enthalpy of formation of the complex of **1** with [70]fullerene.

TABLE 4: Enthalpies and Entropies of Formation of the [70]Fullerene−Calix[6]arene Complexes

complex	ΔH_f^0 (kJ mol^{-1})	ΔS_f^0 (J K^{-1} mol^{-1})
[70]fullerene·**1**	−48 ± 6	−100 ± 20
[70]fullerene·**2**	−25 ± 4	−13 ± 12
[70]fullerene·**3**	−68 ± 10	−158 ± 42

To examine this idea, the HOMO energies of the host (**1**, 8.6865; **2**, 8.6772; and **3**, 8.6708 eV) were evaluated with the PM3 MO calculation. The plot of the HOMO energies against Gibbs energies gave a good linear relationship with a correlation coefficient of 0.92. Haino et al. also offered a similar rationale for the data they have observed with calix[5]arenes.[40]

4. Conclusion

[70]Fullerene is shown to form 1:1 supramolecular complexes with various mono O-substituted calix[6]arenes under study. The $h\nu_{CT}-I_D^v$ dependence has been exploited to determine the degrees of charge transfer of the complexes. The very low values of degrees of charge transfer indicate that the CT complexes studied here have a neutral character in the ground state. Calix[6]arene **2**, in particular, forms an inclusion complex with [70]fullerene as revealed by a higher formation constant value. Thermodynamic parameters have also been determined for the complexes under study, which have shown that a solvophobic effect and $\pi-\pi$ interactions are major driving forces for the complexation process.

Acknowledgment. S.B. thanks the Council of Scientific and Industrial Research, India, for providing a senior research fellowship. Financial assistance by UGC, India, extended through the DSA project in chemistry is also gratefully acknowledged.

References and Notes

(1) Rohlfing, E. A.; Kox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *8*, 13322.

(2) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075.

(3) Lee, K.; Song, H.; Park, J. T. *Acc. Chem. Res.*, **2003**, *36*, 78.

(4) Dinnebier, R. E.; Gunnarsson, O.; Brumm, H.; Koch, E.; Stephens, P. W.; Huq, A.; Jansen, M. *Science* **2002**, *296*, 109.

(5) Iwasa, Y.; Shimoda, H.; Palstra, T. T. M.; Maniwa, Y.; Zhou, O.; Mitani, T. *Phys. Rev. B* **1996**, *53*, 8836.

(6) Wilson, S. R. Biological Aspects of Fullerenes. In *Fullerenes: Chemistry, Physics and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley and Sons: New York, 2000, pp 431−436.

(7) Boltalina, O. V.; Dashkova, E. V.; Sidorov, L. N. *Chem. Phys. Lett.* **1996**, *256*, 253.

(8) Ichida, M.; Sohda, T.; Nakamura, A. *J. Phys. Chem. B* **2000**, *104*, 7082.

(9) Wang, Y.-B.; Lin, Z. *J. Am. Chem. Soc.* **2003**, *125*, 6072.

(10) Guldi, D. M. *Chem. Commun.* **2000**, 321.

(11) Kesti, T.; Tkachenko, N.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *J. Photochem. Photobiolog. Sci*. **2003**, 251.

(12) Scurlock, R. D.; Ogilby, P. R. *J. Photochem. Photobiol., A* **1995**, *91*, 21.

(13) Graja, A.; Semkin, V. N.; Drichko, N. V.; Konarev, D. V.; Lyubovskaya, R. N. *Synth. Met.* **1999**, *103*, 2421.

(14) Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S.; Banerjee, M.; Mukherjee, A. K. *J. Phys. Chem. A* **2002**, *106*, 6710.

(15) Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S.; Banerjee, M.; Mukherjee, A. K. *J. Phys. Chem. B* **2003**, *107*, 11830.

(16) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K., 1989.

(17) *Calixarenes*; Vicene, J., Böhmer, V., Eds.; Kluwer Academic Press: Dordrecht, The Netherlands, 1991.

(18) Coruzzi, M.; Andreetti, G. D.; Bocchi, V.; Pochini, A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1133.

(19) Komatsu, N. *Tetrahedron Lett*. **2001**, *42*, 1733.

(20) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229.

(21) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699.

(22) Atwood, J. L.; Barbour, L. J.; Raston, C. L. *Cryst. Growth Des.* **2002**, *2*, 3.

(23) Cho, Y.; Kim, G.; Lee, S.; Ihm, J. Technical Proceedings of the 2002 International Conference on Computational Nanoscience and Nanotechnology, Nanotech 2002; Vol. 2, pp 291.

(24) Semwal, A.; Bhattacharya, A.; Nayak, S. K. *Tetrahedron* **2002**, *58*, 5287.

(25) Mulliken, R. S. *J. Am. Chem. Soc*. **1952**, *74*, 811.

(26) Sibley, S. P.; Campbell, R. L.; Silber, H. B. *J. Phys. Chem.* **1995**, *99*, 5274.

(27) Georghiou, P. E.; Mizyed, S.; Chowdhury, S. *Tetrahedron Lett.* **1999**, *40*, 611.

(28) Ichida, M.; Sohda, T.; Nakamura, A. *Chem. Phys. Lett*. **1999**, *310*, 373.

(29) Li, J.; Feng, J.; Sun, C. *J. Phys. Chem.* **1994**, *98*, 8636.

(30) Slifkin, M. A. *Charge-Transfer Interactions of Biomolecules*; Academic Press: London & New York, 1971; p 7.

(31) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc*. **1949**, *71*, 2703.

(32) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett*. **1991**, *177*, 394.

(33) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun*. **1990**, 1423.

(34) Harrowfield, J. M.; Mocerino, M.; Skelton, B. W.; Whitaker, C. R.; Write, A. H. *Aust. J. Chem.* **1994**, *47*, 1185.

(35) Ikeda, A.; Kawaguchi, M.; Suzuki, Y.; Hatano, T.; Numata, M.; Shinkai, S. *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *38*, 163.

(36) Shinkai, S.; Ikeda, A. *Gazz. Chim. Ital.* **1997**, *127*, 657.

(37) Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S.; Banerjee, M.; Mukherjee, *Spectrochim. Acta Part A*, in press.

(38) Ikeda, A.; Suzuki, Y.; Yoshimura, M.; Shinkai, S. *Tetrahedron* **1998**, *54*, 2497.

(39) Tao, W.; Barra, M. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1957.

(40) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 259.