

# Evidence of Reverse Micellization of a Calix[4]arene through a Study of Its Charge Transfer and Host–Guest Complexation with [60]Fullerene

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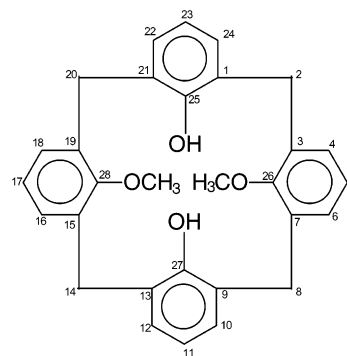
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Received: January 12, 2004; In Final Form: April 10, 2004

By UV–vis absorption and fluorescence spectroscopy it has been established that 25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**1**) forms reverse micelles in CCl<sub>4</sub> and *n*-hexane media. The new feature of this compound as a surfactant is that even before micelle formation it can incorporate water molecules and the critical micellization concentration (cmc) in nonaqueous media increases with increase in  $\omega$  (=water:1 mole ratio). The inclusion complex of **1** with [70]fullerene has a CT absorption band that, in conjunction with those of some quinone complexes of **1**, leads to the determination of the vertical ionization potential of **1**. <sup>1</sup>H NMR spectrometric determination of the formation constant (*K*) of the inclusion complex of [60]fullerene with **1** in CCl<sub>4</sub> has revealed that *K* increases on addition of microquantities of water. This has been rationalized by assuming that the –OH groups of the calix[4]arene molecules attach themselves to the water micropool of the reverse micelles by forming H-bonds and the individual calix[4]arene molecule obtains a conical conformation with a wider rim diameter than that in the absence of water and that this preorganization facilitates inclusion. By utilizing the spectral variation of the [60]fullerene·**1** complex in CCl<sub>4</sub> as the continuous medium with change in  $\omega$ , a critical  $\omega$  (=8) has been found below which the water in the micropool is “bound” and above which “free” water begins to accumulate in the water micropool.

## Introduction

Calix[*n*]arenes<sup>1</sup> behave as a new generation of host molecules after cyclodextrins and crown ethers. On the other hand, supramolecular and charge-transfer complexes of [60]- and [70]fullerenes<sup>2,3</sup> have generated an avalanche of research activity for their potential application in photophysics,<sup>4–7</sup> superconductivity,<sup>8</sup> ferromagnetism,<sup>9</sup> and photo- and biomolecular chemistry.<sup>10,11</sup> The importance of such studies is revealed in a good number of books and review articles.<sup>12–17</sup> The surface chemical activity of some water-soluble hexasulfonated calix[6]arene derivatives has been shown<sup>18</sup> tensiometrically through determination of critical micellization concentration (cmc), and it has been claimed in some cases where no cmc can be found that such molecules behave as “unimolecular micelles”. Water-insoluble calixarenes are, therefore, expected to exhibit surface chemical activity through the formation of “reverse” or “inverted” micelles.<sup>19</sup> To our knowledge, so far no attempt has been made to establish this by a spectroscopic method. The calixarene used in the present study is 25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**1**), which is insoluble in water but soluble in organic solvents with low polarity. A good number of significant works on the synthesis of calix[4]arenes and on the photophysical properties resulting from their complexation with metal ions have been done.<sup>20–24</sup> The purpose of the present work is 3-fold: to see (i) whether the calix[4]arene (**1**) behaves as a donor in forming charge-transfer complexes, (ii) whether it can form reverse micelle in nonaqueous medium by incorporating microquantities of water, and (iii) whether hydrogen-bond formation with water of the reverse micellar micropool



**Figure 1.** Structure of 25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**1**).

on one side of the calixarene rim helps to open up the other rim and thereby promotes the inclusion of [60]fullerene within the calixarene cavity. The present work has another important purpose. From absorption and emission spectroscopic studies with aqueous dye solutions in surfactant/alkane reverse micelles it has been established<sup>25,26</sup> that there is a critical  $\omega$  (i.e., number of moles of water:number of moles of surfactant) for every reverse micellar system below which water in the micropool is “bound” and above which some water molecules with a larger freedom of movement begin to accumulate in the micropool. In the present work an attempt has been made to see whether the spectral variation of the [60]fullerene·**1** inclusion complex in CCl<sub>4</sub> medium can be utilized to obtain such a critical  $\omega$ .

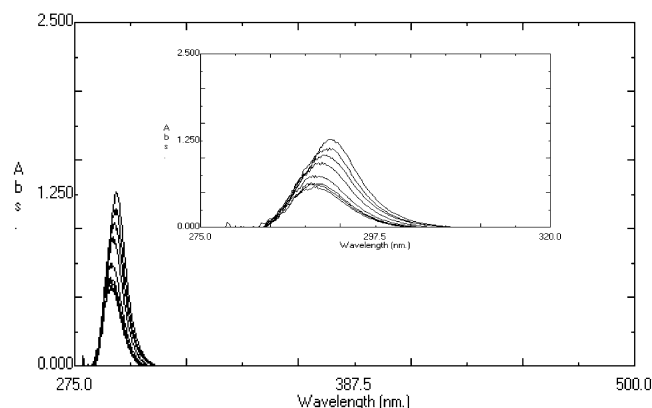
## Materials and Method

25,27-Dihydroxy-26,28-dimethoxycalix[4]arene (**1**), the structure of which is shown in Figure 1, was prepared by the method

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**Figure 2.** Red shift of the calixarene **1** absorption band with increase in concentration (1.191, 1.274, 1.370, 1.635, 2.331, 2.739, 3.320, and 4.058)  $\times 10^{-4}$  mol dm $^{-3}$  (from bottom to top); reference CCl $_4$ . Inset: relevant region expanded.

**TABLE 1: Charge Transfer Absorption Maxima ( $\lambda_{CT}$ ), CT Transition Energy ( $h\nu_{CT}$ ), Vertical Electron Affinity of the Acceptors ( $E_A^v$ ), and Vertical Ionization Potential ( $I_D^v$ ) of the Calix[4]arene **1****

acceptor	$\lambda_{CT}$ , nm	$h\nu_{CT}$ , eV	$E_A^v$ , eV	$10^3 \times \alpha$	$I_D^v$ , eV
<i>o</i> -chloranil	560	2.097	2.87	3.87	7.68
[70]fullerene	480	2.446	2.59	3.71	
2,3-dichloro-1,4-naphthoquinone	494	2.377	2.38	3.59	
menadione	548	2.143	2.18	3.48	

described in ref 27, and the purity of the product was checked by  $^1\text{H}$  NMR. [60]Fullerene was collected from Sigma and [70]fullerene from SES Research Inc., Houston, TX. *o*-Chloranil and 2,3-dichloro-1,4-naphthoquinone were collected from Sigma; they were further purified by sublimation just before use. The other chemical, e.g., menadione (i.e., 2-methyl-1,4-naphthoquinone) was collected from Sigma and was used without further purification. The solvent, carbon tetrachloride, was of UV-spectroscopic grade. This was further purified by keeping it in fused calcium chloride for 24 h and then distilling just before use. Fluorimetric measurement was done in *n*-hexane medium. The commercial, guaranteed, reagent-grade *n*-hexane was further purified by refluxing with metallic sodium for 4 h and then distilling just before use. Absorption data were recorded by a UV 1601 PC model Simadzu spectrophotometer fitted with a Peltier controlled thermobath. Fluorescence intensities were measured by a Hitachi F-4500 fluorescence spectrophotometer.  $^1\text{H}$  NMR spectra of the calixarene-C $_{60}$  mixtures in CCl $_4$  solution were recorded on a Bruker AC-200 (200 MHz) NMR spectrometer with CDCl $_3$  as an internal lock.

## Results and Discussion

**Study of Charge-Transfer Complexation.** In the present study, CT bands were observed in the case of complexes of the calix[4]arene (**1**) with (i) *o*-chloranil, (ii) menadione, (iii) 2,3-dichloro-1,4-naphthoquinone, and (iv) [70]fullerene. To obtain CT bands, a spectrum of each of the solutions (in CCl $_4$ ) containing **1** as donor and the compounds i–iv as acceptor was recorded separately against the pristine acceptor solution as reference. The CT bands in solution were detected by taking a high concentration of the donor (viz., [**1**]  $\approx 10^{-3}$  mol dm $^{-3}$ ) compared to that of each acceptor ( $\approx 10^{-4}$ – $10^{-5}$  mol dm $^{-3}$ ). Values of  $\lambda_{CT}$  are given in Table 1. Compound **1** has a sharp absorption peak at about 290 nm, but it does not absorb above 350 nm and thus does not affect the detection of CT peaks. With [60]fullerene, however, no CT peak could be detected in

**TABLE 2: Variation of Absorbance (in CCl $_4$  Medium) and Fluorescence Intensities (in *n*-Hexane) of the Calix[4]arene **1** with Concentration**

[ <b>1</b> ] $\times 10^4$ (mol dm $^{-3}$ )	absorbance at 291 nm	[ <b>1</b> ] $\times 10^4$ (mol dm $^{-3}$ )	fluorescence intensity (arbitrary units)
5.478	1.2908	5.797	1324
4.058	1.2175	5.041	1280
3.32	1.1128	3.998	1179
2.7391	1.0344	3.623	1178
2.331	0.9232	3.051	1152
2.067	0.8905	2.828	1110
1.826	0.796	2.635	1077
1.635	0.702	2.467	1045
1.4806	0.6318	2.319	999.6
1.3695	0.6071	2.188	964.1
1.274	0.567		
1.1904	0.5311		
5.797	1.4156		

this way; only the well-known broad absorption band of [60]fullerene showed an overall increase in intensity on adding the solution of calixarene **1**. The vertical electron affinities ( $E_A^v$ ) of the acceptors i and ii were collected from the literature<sup>28–31</sup> and those of the other two have been recently determined.<sup>32,33</sup> These  $E_A^v$  values correlate well with the presently observed CT transition energies ( $h\nu_{CT}$ , Table 1) in accordance with the Mulliken<sup>34</sup> theory. The method for determination of the vertical ionization potential ( $I_D^v$ ) of the donor on the basis of this theory requires the working formula

$$2C_1 + h\nu_{CT} = C_1(C_1 + h\nu_{CT})/I_D^v + C_2/I_D^v + I_D^v \quad (1)$$

which was used in some of our previous works.<sup>33</sup> The present experimental CT transition energies (Table 1) gave the following linear regression equation:

$$2C_1 + h\nu_{CT} = (0.13 \pm 0.005)[C_1(C_1 + h\nu_{CT})] + (7.84 \pm 0.284) \quad \text{correln coeff} = 0.99 \quad (2)$$

From this correlation,  $I_D^v$  of compound **1** is found to be 7.68 eV (according to the procedure explained in ref 33). The degrees of charge transfer ( $\alpha$ ) in the ground state of the complexes were calculated by a method adopted in ref 35. The values of  $\alpha$  are low and, as expected with a fixed donor,  $\alpha$  increases with increase in the electron affinity of the acceptors (Table 1).

**Self-Aggregation of the Calix[4]arene **1** and Determination of Cmc.** Electronic absorption spectra of the calixarene **1** in CCl $_4$  at a number of concentrations are shown in Figure 2. It is observed that with an increase in concentration not only does the absorbance increase but there is also a gradual red shift of the absorption maximum (near 290 nm). Such red shifts are indication of molecular self-aggregation.<sup>36</sup> The variation of absorbance (at 291 nm) with concentration is shown in Figure 3a (Table 2), where there are clearly two distinct parts, but since the slopes in the two parts do not differ much, we apply the method described in ref 36. The absorbance ( $A$ ) values in the lower concentration region are subjected to the linear fit

$$A = a + bC \quad (3)$$

where  $C$  is the concentration of **1**. Using the best fit value of  $a$  and  $b$ , we plotted  $A - (a + bC)$  against  $C$ . Before micellization the ordinate is expected to be zero and then a break point should be obtained at the cmc. Figure 3b shows such a plot in which a clear break point indicates micellization. The same cmc value is also obtained from fluorescence data (Table 2) recorded in *n*-hexane medium; after excitation at 286 nm, the calixarene **1**

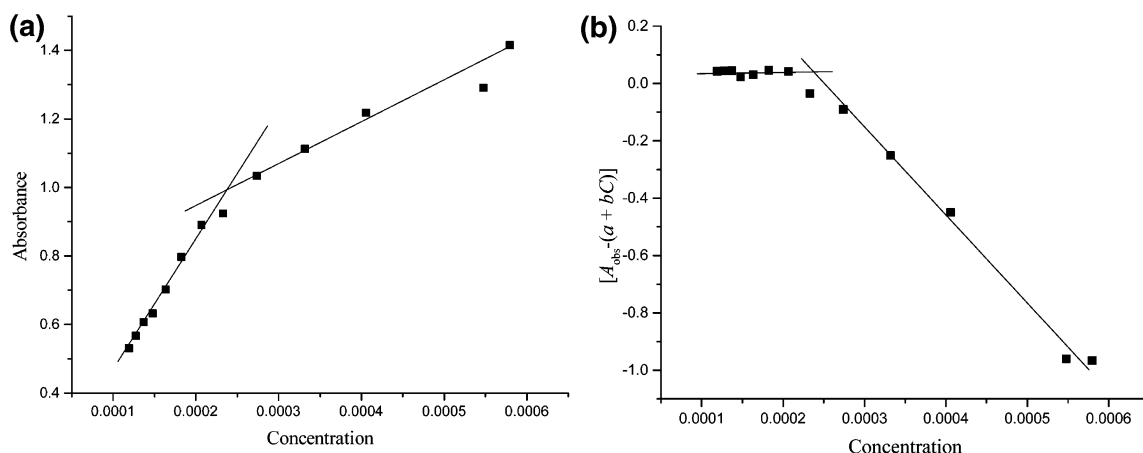


Figure 3. Plots for determination of cmc by the absorption spectrometric method.

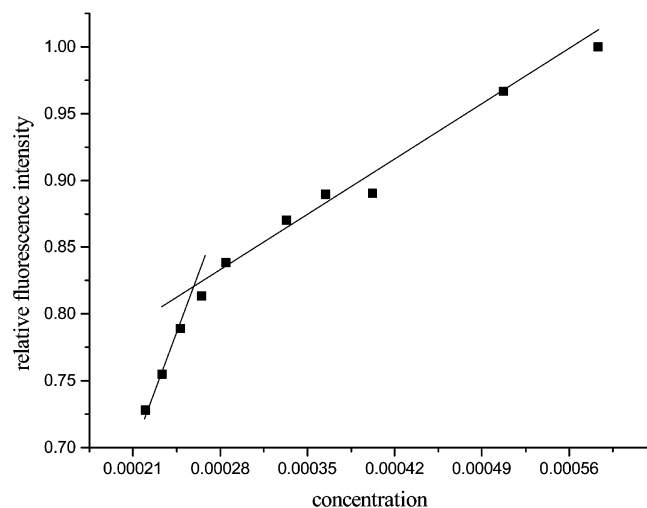


Figure 4. Plot of relative fluorescence intensity against concentration of **1** for determination of cmc. The observed intensities ( $I$ ) of emission in arbitrary units were normalized to  $I_{\text{mas}} = 1.0$ .

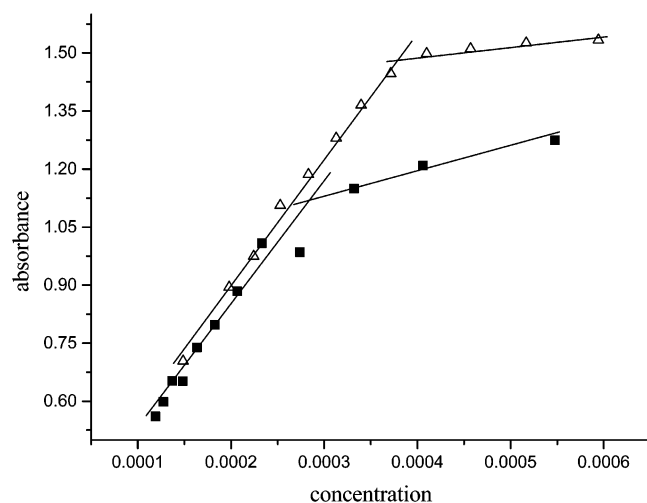


Figure 5. Plots for determination of cmc at  $\omega = 10$  (dark square) and 27 (hollow triangle).

emits at 302 nm, and when the emission intensities (normalized by taking the maximum intensity to be unity) are plotted against the concentration of **1**, a break point is obtained (Figure 4) indicating the same value of cmc as obtained by absorption measurement. Since the medium is nonpolar, such micelles are “reverse” or “inverted” micelles,<sup>19</sup> with the polar –OH groups pointing inward and the nonpolar part exposed to the bulk

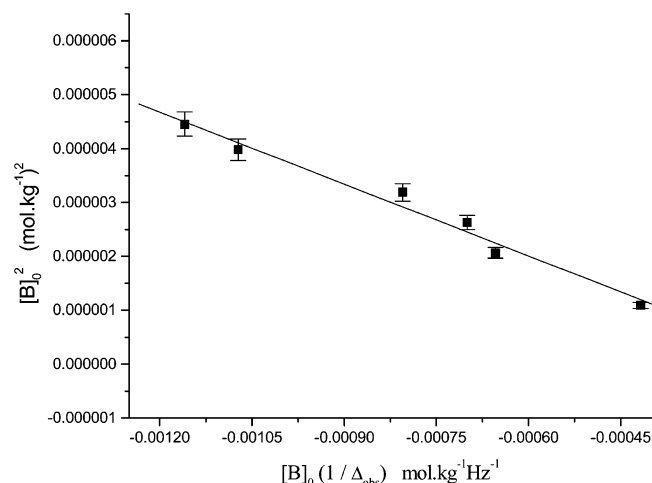
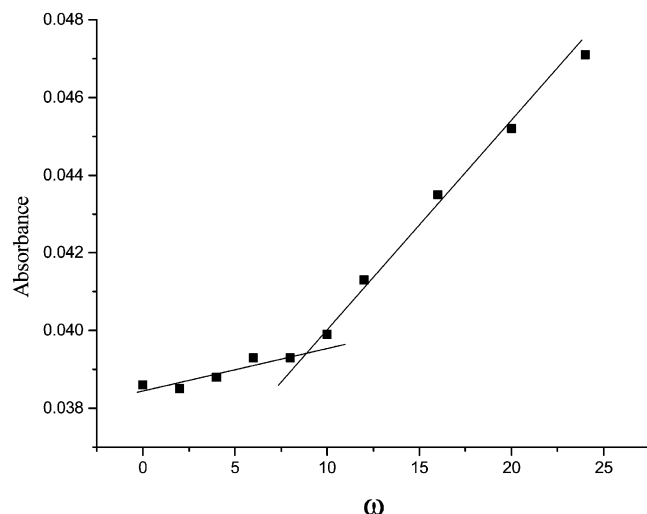


Figure 6. Plot according to eq 11 in the presence of water ( $\omega = 2$ ).

TABLE 3: NMR Chemical Shifts of the –OMe Protons in Calixarene **1**–[60]Fullerene Mixtures in  $\text{CCl}_4$  Medium at Varying Concentrations of **1** in the Absence and Presence of Water at 298 K

$\omega$	$10^5 \times [A]_0$ (mol kg <sup>-1</sup> )	donor concn $\times 10^3$ (mol kg <sup>-1</sup> )	$\Delta_{\text{obs}}$ , Hz	$10^{-5} \times K$ (kg mol <sup>-1</sup> )
0	1.810	0.974	–1.92	3.7
		1.252	–2.00	
		1.461	–2.20	
		1.647	–2.08	
		1.786	–2.20	
		1.925	–2.04	
		2.041	–2.20	
		2.111	–1.82	
2	2.426	1.044	–2.50	15.2
		1.438	–2.20	
		1.623	–2.32	
		1.786	–2.22	
		1.994	–1.86	
		2.111	–1.82	

solvent. Measurement of absorbance at 291 nm was also carried out by adding microliter quantities of water to the  $\text{CCl}_4$  solutions of **1** using a Hamilton microsyringe and maintaining a fixed  $\omega$  (=number of moles of water: number of moles of surfactant, here calixarene **1**). It was observed that upon addition of water the two parts in the absorbance vs concentration plot have widely different slopes and the cmc could be detected from such simple plots (Figure 5) without resorting to the difference plot described in ref 36. This is consistent with the known fact that the presence of a microquantity of water in the system facilitates reverse micellization. Values of cmc determined in this way at  $\omega = 0$ ,



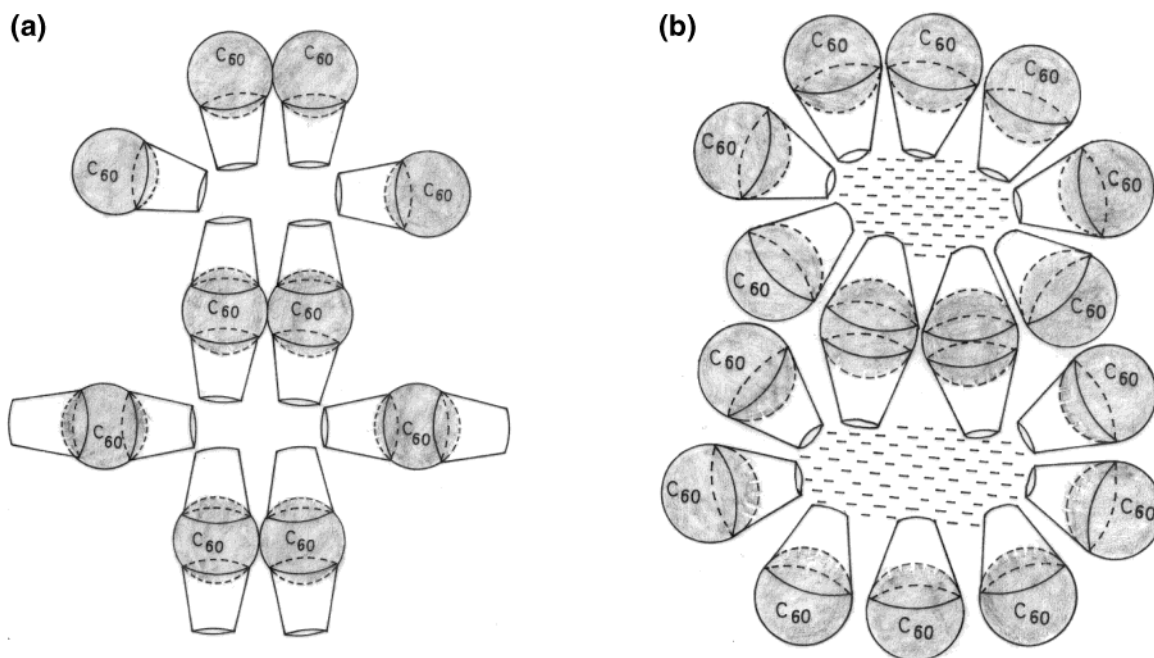
**Figure 7.** Variation of absorbance of the [60]fullerene·**1** complex in  $\text{CCl}_4$  medium at 532 nm with change in  $\omega$ . (Reference  $\text{CCl}_4$ ; concentration of [60]fullerene =  $3.704 \times 10^{-5} \text{ mol dm}^{-3}$  and [calixarene **1**] =  $1.327 \times 10^{-3} \text{ mol dm}^{-3}$ ).

10, 19, and 27 were found to be 0.24, 0.27, 0.29, and 0.37  $\text{mmol dm}^{-3}$ , respectively. This increase in cmc with  $\omega$  may be explained as follows: Initially the added water molecules are incorporated in the cavity of calixarene **1** and some water molecules make hydrogen bonds with the  $-\text{OH}$  groups in the lower rim, leading to a conical conformation. The narrower side requires less space for aggregation and this results in an increase in cmc. When more water molecules are added, the size of the water micropool increases, leading thereby to a further increase in cmc with  $\omega$ . A further support to the hypothesis that the calixarene **1** aggregates to form reverse micelle is furnished as follows:

The aggregation equilibrium is represented as



where  $S$  denotes the monomer and  $S_n$  the  $n$ -mer of the surfactant.



**Figure 8.** A model for reverse micelles of calixarene **1** helping 1:2 complex formation in the (a) absence and (b) presence of water.

The total absorbance ( $A$ ) of the equilibrium mixture is given by

$$A = \epsilon ([S]_T - n[S_n]) + \epsilon' [S_n] \quad (5)$$

where  $\epsilon$  and  $\epsilon'$  are the molar absorptivities of the monomer and  $n$ -mer respectively,  $[S]_T$  is the total concentration of the surfactant (here, compound **1**), and  $[S_n]$  is the  $n$ -mer concentration. Equation 5 can be rearranged as

$$A - [S_{\text{cmc}}]\epsilon = \frac{\epsilon'}{n} ([S]_T - [S_{\text{cmc}}]) \quad (6)$$

$\epsilon$  is obtained from a Beer's law plot of absorbance against concentrations below the cmc (i.e., from the value of  $b$  in eq 3). Now according to eq 6 a plot of  $A - [S_{\text{cmc}}]\epsilon$  against  $([S]_T - [S_{\text{cmc}}])$  should be a straight line through the origin with a slope equal to  $\epsilon'/n$ . The present experimental data confirmed this, the regression equation being

$$A - [S_{\text{cmc}}]\epsilon = (1242 \pm 46)([S]_T - [S_{\text{cmc}}]) + (0.02 \pm 0.01) \quad (7)$$

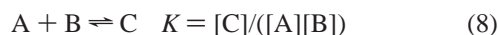
The correlation coefficient of the regression was 0.999. The nonzero intercept in eq 7 is very small in magnitude and is due to unavoidable experimental error.

#### Host–Guest Complexation with [60]Fullerene in the Absence and Presence of Water by NMR Spectrometry.

To determine the formation constant ( $K$ ) of a molecular complex  $C$  between the molecules  $A$  and  $B$ , one requires a knowledge of the equilibrium concentrations of the species  $A$ ,  $B$ , and  $C$ . In host–guest complexation, two possible stoichiometries, viz., 1:1 and 1:2 guest:host, have so far been reported;<sup>37–42</sup> probably the single exceptional case<sup>43</sup> is the complex of [60]fullerene (guest) with hydroquinone (host), where the reported stoichiometry is 1:3 guest:host. With the present experimental data, we have tried the common two cases,



viz., 1:1 and 1:2, the corresponding equilibria being



and



[60]Fullerene has no proton, so the formation equilibrium of the [60]fullerene–calixarene complex has been studied in the present report on the basis of changes in chemical shift of B protons on complexation; the derivation of the working formula for 1:1 stoichiometry was discussed in one of our earlier publications:<sup>42</sup>

$$[B]_o = \Delta_o[A]_o(1/\Delta_{obs}) - 1/K \quad (10)$$

For 1:2 fullerene:calixarene stoichiometry, the working formula, by a similar reasoning as in ref 42, becomes

$$[B]_o^2 = \Delta_o[A]_o[B]_o(1/\Delta_{obs}) - 1/K \quad (11)$$

In eqs 10 and 11,  $\Delta_{obs} = \delta_{obs}^B - \delta_o^B$  = the observed chemical shift of a B-proton in the equilibrium mixture of A and B relative to that in free B and  $\Delta_o = \delta_c^B - \delta_o^B$  = the chemical shift of the same B-proton in the pure complex relative to that in the free B molecule. Thus with a constant  $[A]_o$ , a linear plot of  $[B]_o$  against  $1/\Delta_{obs}$  is expected for 1:1 stoichiometry, and for the 1:2 case, the plot should be linear with  $[B]_o^2$  against  $[B]_o/\Delta_{obs}$ . From the intercept and slope of such plots  $K$  and  $\Delta_o$  can be evaluated. Experimental data for  $\Delta_{obs}$  at a number of concentrations of B keeping that of A fixed are shown in Table 3. The experiment was carried out in  $CCl_4$  medium in the absence of water ( $\omega = 0$ ) and also by adding a microquantity of water to the same series of  $CCl_4$  solutions using a Hamilton microsyringe (so as to adjust  $\omega = 2$ ). With a fixed concentration of [60]fullerene, the observed  $\Delta$  decreases as the donor concentration increases. In both cases ( $\omega = 0$  and  $\omega = 2$ ), excellent linear plots in accordance with eq 11 were obtained, one typical plot being shown in Figure 6. When eq 10 was tried for 1:1 stoichiometry, the plots were scattered, showing no linear trend. Thus, under the present experimental conditions the host–guest complex is of 1:2 fullerene:calixarene **1** stoichiometry. Results of regression analysis and values of  $K$  and  $\Delta_o$  obtained therefrom are shown in Table 3. It was found that  $K$  increases appreciably on addition of water. The value of  $K$  at  $\omega = 2$  is about 4 times that at  $\omega = 0$ .

**State of Water in the Micropool from Spectral Variation of the Host–Guest Complex.** It is known<sup>25,26</sup> from absorption and emission spectrometric studies with aqueous solutions of dyes in a reverse micellar system that the water pool environment in reverse micelles changes with change in  $\omega$ , exhibiting a critical  $\omega$  above which the water in the micropool has greater freedom of movement. For a similar purpose we have utilized in the present work the spectral variation of the [60]fullerene·**1** complex in  $CCl_4$  as the continuous medium with change in  $\omega$ . When water was gradually added to a mixture of  $CCl_4$  solutions of [60]fullerene and calixarene **1** above its cmc, the solution remained clear and the intensity of the broad absorption band of [60]fullerene in the visible range showed a systematic increase in intensity, indicating better complexation on addition of water. Absorbance data at 532 nm (somewhere at the middle of the broad fullerene band), when plotted against  $\omega$  (Figure 7), shows that there is a critical  $\omega$  ( $\approx 8$ ) for the calixarene **1**– $CCl_4$  reverse micellar system below which the water in the micropool is

“bound” and above which “free” water begins to accumulate in the water micropool.

## Conclusion

At concentrations above cmc, the calixarene **1** forms with [60]fullerene a host–guest complex of 1:2 stoichiometry that may be modeled (Figure 8a) as a bicapped complex resulting from the close proximity of the reverse micellar aggregates. Addition of water creates a polar micropool that helps to open up the wider rim (Figure 8b) by pulling in the –OH groups by H-bond formation. A remarkable increase in the formation constant ( $K$ ) on addition of a microquantity of water is thus observed.

**Acknowledgment.** A.S. thanks the CSIR, India, for a junior research fellowship. Financial assistance by the UGC, New Delhi, extended through the DSA project in Chemistry, The University of Burdwan, is also gratefully acknowledged.

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