Spectrophotometric and thermodynamic study of supramolecular complexes of [60]- and [70]fullerenes with a number of calix[n]arenes

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[60]- and [70]fullerene have been shown to form 1 : 1 supramolecular complexes with (i) 49,50,51,52,53,54,55,56-octamethoxy-5,11,17,23,29,35,41,47-octa(4-*tert*-butyl)calix[8]arene (**1**), (ii) 37,38,39,40,41,42-hexamethoxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**2**) and (iii) 37,39,41-trimethoxy-38,40,42-trihydroxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**3**) in three different solvents, namely CCl_4, toluene and *o*-xylene, by electronic absorption spectroscopy. Charge transfer absorption bands of the complexes have been identified in CCl_4 from which ionisation potentials of the calixarenes have been obtained. Isosbestic points have been found in the cases of $C_{60} \cdot 1$ and $C_{60} \cdot 2$ complexes in toluene and *o*-xylene. Formation constants of the complexes have been determined at four different temperatures from which the enthalpies and entropies of formation of the complexes have been obtained. Moreover, the formation constant of $C_{60} \cdot 3$ is higher than that of $C_{60} \cdot 2$ at all of the four temperatures studied. This has been rationalised in terms of a high degree of preorganisation of the host **3** through intramolecular H-bonding at its lower rim.

1 Introduction

Supramolecular chemistry involving the filling up of calix-[*n*]arene[1,2] baskets by fullerene[3] balls is not only a topic of current academic interest—studies along these lines have led to some very significant practical applications.[4–9] For example Atwood *et al.*[4] and Shinkai *et al.*[5] have shown that *p*-*tert*-butylcalix[8]arene selectively sequesters [60]fullerene from a mixture containing [60]- and [70]fullerene. It is, therefore, necessary to carry out thermodynamic studies on the complexation of [60]- and [70]fullerenes as host with calix[*n*]arene derivatives as guest. Danil de Nemor *et al.*[10] have published an extensive review of the thermodynamics of host–guest complexation with calix[*n*]arene derivatives. However most of the data concern polar organic solvents. Shinkai *et al.*[11] were the first to report the formation constant of the complexes of C_{60} with calix[*n*]arene derivatives having (arylamino)alkyl moieties at the upper rim and subsequently they determined the enthalpy (ΔH_f°) and entropy (ΔS_f°) of complexation of the system. More recently, C_{60}–calix[*n*]arene host–guest complexation has been studied[12] and 1 : 1 stoichiometry of the complexes of C_{60} with calix[4]naphthalenes has been established.[13] Thermodynamic data on these complexes have also been reported.[14] Although absorption spectroscopy has been used in these studies, the charge transfer (CT) absorption band of the complexes has not been detected. In the present paper we report the CT absorption bands of the complexes of C_{60} and C_{70} with (i) 49,50,51,52,53,54,55,56-octamethoxy-5,11,17,23,29,35,41,47-octa(4-*tert*-butyl)calix[8]arene (**1**), (ii) 37,38,39,40,41,42-hexamethoxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**2**) and (iii) 37,39,41-trimethoxy-38,40,42-trihydroxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**3**) in CCl_4. Structures of **1**, **2** and **3** are shown in Fig. 1. From the observed CT bands the ionisation potentials (I_D) of the calixarenes under study have been determined. Moreover the formation constants of the complexes have been determined at four different temperatures in three different solvents, *viz.*, CCl_4, toluene and *o*-xylene for estimating enthalpies and entropies of the complexation processes.

2 Materials and methods

[60]Fullerene was obtained from Sigma. [70]Fullerene was obtained from SES Research Corporation, USA. Calixarenes were prepared according to the methods in ref. 15 and 16 and their purity was checked by NMR spectra of the purified samples. The solvents CCl_4, toluene and *o*-xylene were of HPLC grade. All optical measurements were done on a Shimadzu UV 2101 PC model spectrophotometer fitted with a TB 85 thermo bath.

3 Results and discussion

3.1 Determination of vertical ionisation potentials (I_D') of the calixarenes

Fig. 2 shows the electronic absorption spectrum of C_{60} in CCl_4 against the solvent as reference. In the same figure, the absorption spectra of two mixtures, one containing **2** and C_{60} and the other containing **3** and C_{60} in CCl_4 are shown. In the latter two cases, C_{60} at the same concentration as that in the mixture was taken as reference (the calixarenes do not absorb in the 360–750 nm range) and it was found that the broad 420–700 nm absorption band of C_{60}, attributable to some of its forbidden singlet–singlet transitions,[17,18] was almost completely masked (due to [60]fullerene in reference) while a new band due to charge transfer (CT) absorption of electron donor–acceptor (EDA) complexes appeared. Fig. 3 shows the electronic absorption spectrum of two mixtures containing **1** + C_{70} and **2** + C_{70} against C_{70} as reference in CCl_4. In these cases new absorption
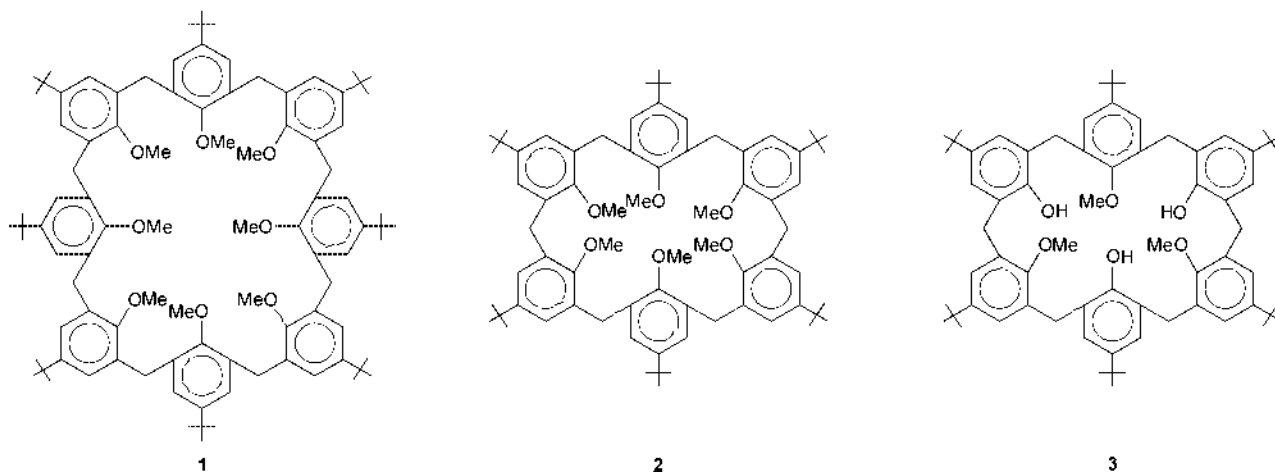
DOI: 10.1039/b106859h
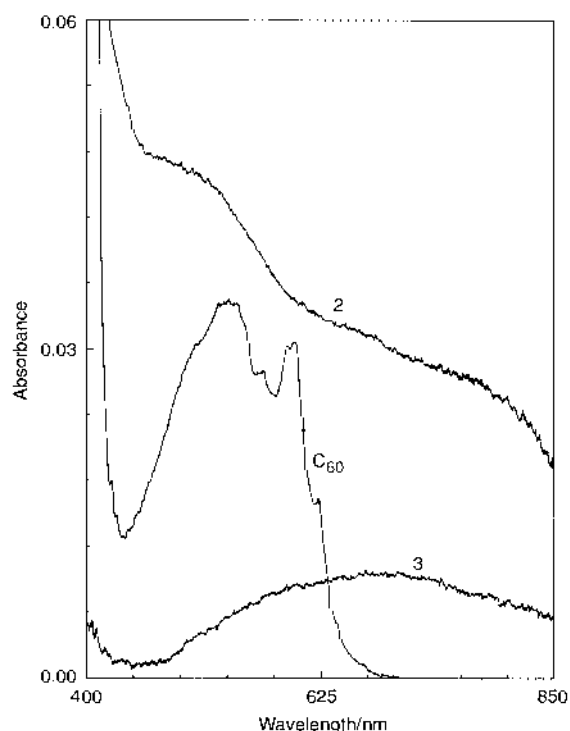
Fig. 1 Structure of **1**, **2** and **3**.

Fig. 2 Absorption spectra of C_{60} in CCl_4 (against the solvent as reference) and mixtures containing C_{60} (7.083×10^{-5} mol dm^{-3}) and **2** (7.12×10^{-3} mol dm^{-3}) and C_{60} (7.215×10^{-5} mol dm^{-3}) and **3** (4.97×10^{-3} mol dm^{-3}) against the respective C_{60} solutions.

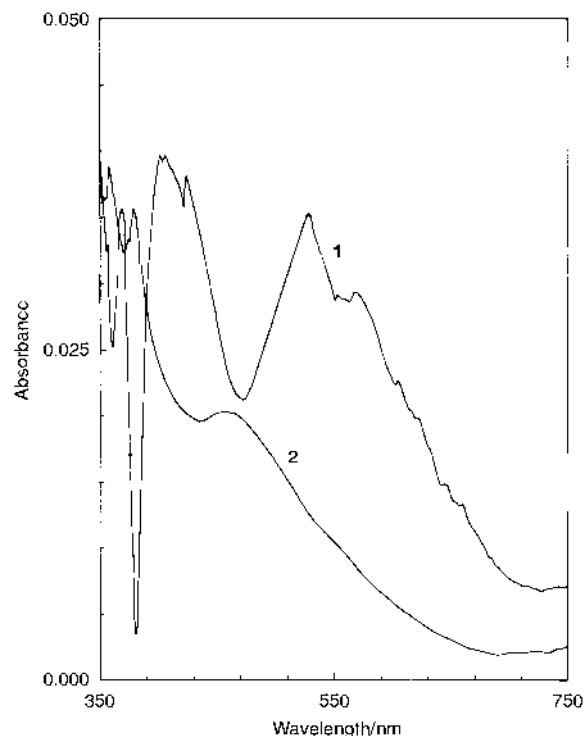**Fig. 3** Absorption spectra of mixtures containing C_{70} (3.553×10^{-5} mol dm^{-3}) and **1** (0.746×10^{-3} mol dm^{-3}) and C_{70} (1.020×10^{-6} mol dm^{-3}) and **2** (1.25×10^{-3} mol dm^{-3}) in CCl_4 solutions against the respective C_{70} solutions.

bands different from that of C_{70} and attributable to charge transfer complex formation appeared too. It may be mentioned at this point that in a recent study on the complexation of calix[4]naphthalenes with C_{60}, no CT band was reported to be observed. The reason is that the CT band intensity is low, and requires the concentration of donor to be much higher than that of the acceptor. In ref. 13 and 14 the concentration of calix[4]naphthalene was 10^{-4} mol dm^{-3} but in the present study the mixture is ~10^{-3} mol dm^{-3} with respect to the calixarenes in each case. The wavelengths at the CT absorption maxima and the corresponding transition energies (hv_{CT}) are summarised in Table 1. In the cases of $C_{60}\cdot$**2** and $C_{70}\cdot$**1** complexes multiple CT peaks were observed. While calculating hv_{CT} the longest wavelength peak was considered. The CT transition energies of EDA complexes of C_{60} with two series of donors of known vertical ionisation potentials (I_D^v), *viz.*, (i) methylbenzenes[19] and (ii) polynuclear aromatic hydrocarbons (PAH)[20] have, according to Mulliken's theory,[21] the correlations given in eqn. (1a) and (1b).

Table 1 CT transition energies of the complexes of C_{60} and C_{70} with **1**, **2** and **3** in CCl_4 solution and ionisation potentials of the donors

Donors	hv_{CT}/eV of the acceptors		I_D/eV of the donors
	C_{60}	C_{70}	
1	1.492	3.492	6.81
2	1.570	4.329	6.85
3	1.810	—	7.20

$$hv_{CT} \,(C_{60}\text{–methylbenzene}) =$$
$$1.235 I_D^v - 6.924; \text{ corrln. coefficient} = 0.85 \quad (1a)$$

$$hv_{CT} \,(C_{60}\text{–PAH}) =$$
$$0.791 I_D^v - 3.877; \text{ corrln. coefficient} = 0.86 \quad (1b)$$

The transition energies of the C_{60}–calixarene complexes observed in the present work when put into eqn. (1a) and (1b), yield two almost equal values of I_D for each of the calixarenes,

Table 2 Absorbance data for mixtures containing $C_{70} + 1$ and $C_{70} + 2$ in toluene

Donor (D)	$10^5[C_{70}]_0$/mol dm^{-3}	Temperature/K	$10^3[D]_0$/mol dm^{-3}	Absorbance at 472 nm
1	1.152	297	0.760	0.216
			1.270	0.197
			1.540	0.194
			2.295	0.188
			2.530	0.215
			2.540	0.202
2	1.152	294	1.890	0.269
			3.135	0.260
			3.480	0.266
			4.712	0.264
			3.473	0.275
			5.892	0.277
			5.650	0.270

Table 3 Absorbance data for mixtures containing $C_{60} + 1$ and $C_{60} + 2$ in toluene

Donor (D)	$10^4[C_{60}]_0$/mol dm^{-3}	Temperature/K	$10^3[D]_0$/mol dm^{-3}	Absorbance at 535 nm
1	1.375	303	0.952	0.194
			1.340	0.173
			1.902	0.198
			2.850	0.197
			3.039	0.188
			3.820	0.191
			4.005	0.197
2	3.251	302	1.414	0.161
			2.119	0.207
			3.075	0.155
			2.848	0.200
			4.012	0.189
			4.731	0.185

as summarized in Table 1. It is noteworthy that as the number of methoxy groups increases, ionisation potential decreases.

3.2 Determination of formation constants (K)

Owing to low intensity of the CT peaks, variation of their intensity with change in donor concentration could not be employed to determine stoichiometry and formation constants (K) of the complexes. Instead, it was observed that the intensity of the broad absorption band of C_{60} and C_{70} (measured against the solvent as reference), was perturbed systematically with gradual addition of the calixarene donors (**1**, **2** and **3**). This phenomenon was utilized to determine the value of K by using the Benesi–Hildebrand (BH)[22] equation for cells with 1 cm optical path length [eqn. (2a) and (2b)].

$$[A]_0[D]_0/d' = [D]_0/\varepsilon' + 1/K\varepsilon' \qquad (2a)$$

$$d' = d - d_A{}^\circ - d_D{}^\circ \qquad (2b)$$

Here $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor respectively, d is the absorbance of the donor–acceptor mixture at the center of the respective perturbed broad peaks of C_{60} and C_{70} measured against the solvent as reference; $d_A{}^\circ$ and $d_D{}^\circ$ are the absorbances of the acceptor and donor solutions with the same molar concentrations as in the mixture at the wavelength of measurement. The quantity $\varepsilon' = \varepsilon_c - \varepsilon_A - \varepsilon_D$ is the corrected molar absorptivity of the complex and ε_A and ε_D are those of the acceptor and the donor respectively at the wavelength of measurement. Here ε_c means the molar absorptivity of the pure complex measured against the solvent as reference. K is the formation constant of the complex. Eqn. (2a) is valid[22] under the condition $[D]_0 \gg [A]_0$ for the 1 : 1 donor–acceptor complex. Experiments were carried out under this condition in CCl_4, toluene and o-xylene at a number of temperatures. Some typical absorbance data are given in Tables 2 and 3. Similar data were obtained at three other temperatures
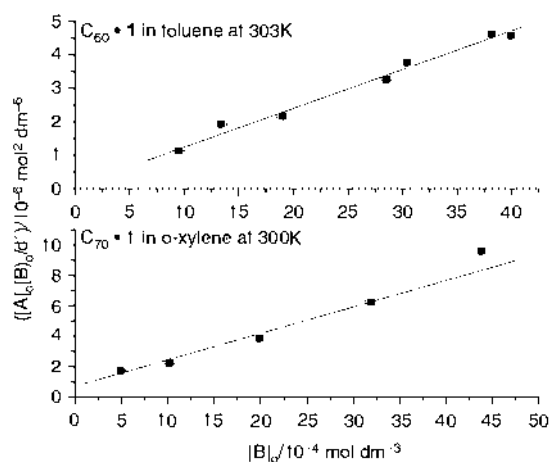
Fig. 4

for all the solvents. In all the cases very good linear plots according to eqn. (2a) were obtained, two typical cases being shown in Fig. 4. In the cases of $C_{70}\cdot\mathbf{1}$ and $C_{70}\cdot\mathbf{2}$, isosbestic points were observed in toluene and o-xylene (one case being shown in Fig. 5). Formation constants determined from the BH plots at four different temperatures are summarized in Tables 4–6.

3.3 Enthalpies (ΔH_f°) and entropies of formation (ΔS_f°) of the complexes of C_{60} and C_{70} with 1, 2 and 3

The enthalpies (ΔH_f°) and entropies of formation (ΔS_f°) of the complexes have been determined by using the van't Hoff equation. As measured, these terms will represent the net change in enthalpy and entropy for the solvated species.

Plots of ln K vs. $1/T$ for the complexes of C_{60} and C_{70} with **1**, **2** and **3** in all the three solvents are linear and have positive slopes.

The linear regression relations are given in eqn. (3a)–(3l).

Table 4 Formation constants (K/dm^3 mol^{-1}) and thermodynamic parameters for complexes of C$_{70}$ with **1** and **2** in three different solvents at a number of temperatures

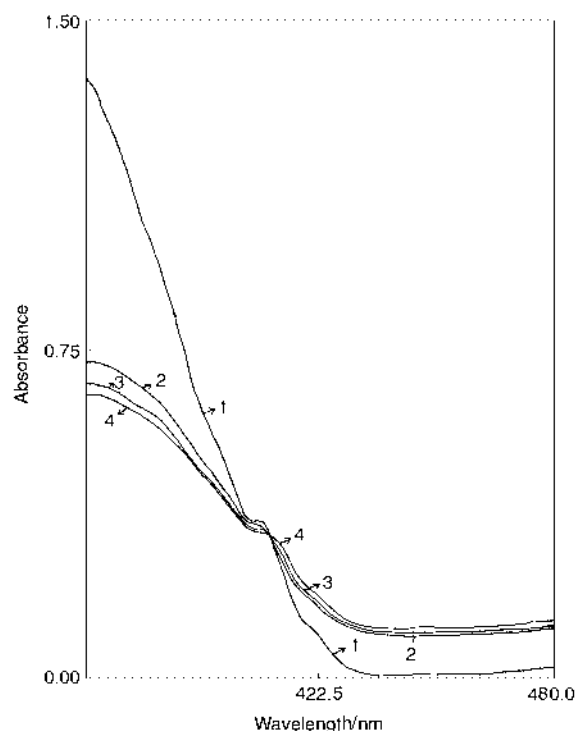| Donor	Solvent	Temp./K	K	ΔH_f°/kJ mol^{-1}	ΔS_f°/J K^{-1} mol^{-1}
1	CCl$_4$	292	3380	-44 ± 3	-82 ± 10
		297	2660		
		308	1265		
		313	1075		
	Toluene	297	15810	-60 ± 17	-120 ± 55
		308	11360		
		315	6825		
		323	2100		
	o-Xylene	300	7800	-120 ± 10	-340 ± 30
		308	1870		
		315	920		
		323	215		
2	CCl$_4$	300	5590	-80 ± 20	-200 ± 65
		308	2950		
		315	710		
		323	690		
	Toluene	294	6490	-180 ± 20	-545 ± 70
		300	1470		
		308	120		
		315	60		
	o-Xylene	300	705	-57 ± 10	-135 ± 35
		308	366		
		315	175		
		323	153		

Fig. 5 Absorption spectra of (1) C$_{70}$ (8.254×10^{-5} mol dm^{-3}); (2) C$_{70}$ (8.254×10^{-5} mol dm^{-3}) + **1** (5.712×10^{-4} mol dm^{-3}); (3) C$_{70}$ (8.254×10^{-5} mol dm^{-3}) + **1** (1.215×10^{-3} mol dm^{-3}); and (4) C$_{70}$ (8.254×10^{-5} mol dm^{-3}) + **1** (3.186×10^{-3} mol dm^{-3}) in o-xylene against the solvent as reference.

For C$_{60}$·**1** in CCl$_4$:

$\ln K = (7940 \pm 520)/RT - (18 \pm 2)$; corrl. coeff. = 0.99 (3a)

For C$_{60}$·**1** in toluene:

$\ln K = (7801.1 \pm 1613.0)/RT - (16.7 \pm 5.2)$;
corrl. coeff. = 0.96 (3b)

For C$_{60}$·**1** in o-xylene:

$\ln K = (6803.0 \pm 548.4)/RT - (12.2 \pm 1.8)$;
corrl. coeff. = 0.99 (3c)

For C$_{60}$·**2** in CCl$_4$:

$\ln K = (5410 \pm 670)/RT - (13 \pm 2)$; corrl. coeff. = 0.96 (3d)

For C$_{60}$·**2** in toluene:

$\ln K = (9993.0 \pm 812.3)/RT - (24.5 \pm 2.62)$;
corrl. coeff. = 0.99 (3e)

For C$_{60}$·**2** in o-xylene:

$\ln K = (3002.1 \pm 593.9)/RT - (0.6 \pm 1.9)$.
corrl. coeff. = 0.96 (3f)

For C$_{70}$·**1** in CCl$_4$:

$\ln K = (5256.1 \pm 345.0)/RT - (9.8 \pm 1.1)$;
corrl. coeff. = 0.99 (3g)

For C$_{70}$·**1** in toluene:

$\ln K = (7122.0 \pm 2008.5)/RT - (14.1 \pm 6.5)$;
corrl. coeff. = 0.93 (3h)

For C$_{70}$·**1** in o-xylene:

$\ln K = (14557.0 \pm 1138.8)/RT - (39.6 \pm 3.6)$;
corrl. coeff. = 0.99 (3i)

For C$_{70}$·**2** in CCl$_4$:

$\ln K = (9744.5 \pm 2402.4)/RT - (23.8 \pm 7.7)$;
corrl. coeff. = 0.94 (3j)

For C$_{70}$·**2** in toluene:

$\ln K = (21849.9 \pm 2541.4)/RT - (65.6 \pm 8.4)$;
corrl. coeff. = 0.99 (3k)

For C$_{70}$·**2** in o-xylene:

$\ln K = (6854.2 \pm 1238.1)/RT - (16.3 \pm 3.9)$;
corrl. coeff. = 0.97 (3l)

The positive slope in each case indicates that the complexation process is exothermic and thus driven by favourable enthalpy changes. The ΔH_f° and ΔS_f° values of the complexes in three solvents are listed in Tables 4 and 5. A linear relationship

Table 5 Formation constants (K/dm^3 mol^{-1}) and thermodynamic parameters for complexes of C_{60} with **1** and **2** in three different solvents at a number of temperatures

	Donor	Solvent	Temp./K	K	ΔH_f°/kJ mol^{-1}	ΔS_f°/J K^{-1} mol^{-1}
	1	CCl$_4$	292	6060	-65 ± 5	-155 ± 15
			302	2720		
			311	1330		
			318	625		
		Toluene	294	16610	-65 ± 15	-140 ± 45
			303	7500		
			310	6310		
			317	2060		
		o-Xylene	295	46790	-55 ± 5	-1000 ± 15
			302	32690		
			310	16450		
			317	9600		
	2	CCl$_4$	292	270	-45 ± 5	-110 ± 20
			304	115		
			313	90		
			323	40		
		Toluene	292	14470	-85 ± 7	-205 ± 20
			302	5060		
			310	2410		
			317	1050		
		o-Xylene	293	14890	-25 ± 5	-5 ± 2
			304	9290		
			313	8990		
			323	5310		

Table 6 Formation constants (K/dm^3 mol^{-1}) and thermodynamic parameters for complexes of C_{60} with **3** in CCl$_4$ at a number of temperatures

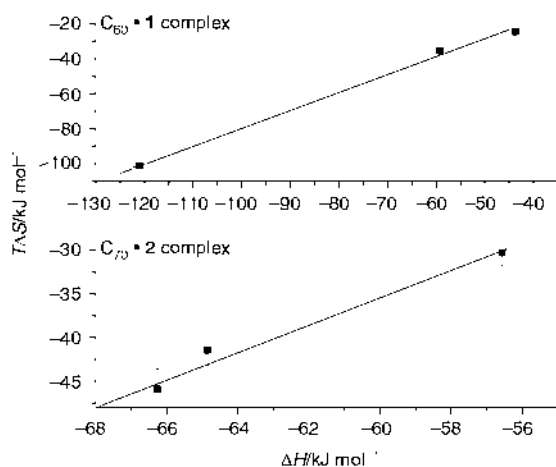| Donor	Temp./K	K	ΔH_f°/kJ mol^{-1}	ΔS_f°/J K^{-1} mol^{-1}
3	292	12420	-75 ± 7	-180 ± 20
	303	3690		
	313	2075		
	319	550		

Fig. 6 $T\Delta S$ vs. ΔH plot for $C_{60} \cdot \mathbf{1}$ and $C_{70} \cdot \mathbf{2}$ systems.

exists between $T\Delta S_f^\circ$ and ΔH_f° for all the complexes under study [eqn. (4a)–(4d)].

Two typical plots are shown in Fig. 6. Such linear relationships are commonly referred to as the compensation effect[23–25] in host–guest complexation. The high positive intercepts indicate that the complexation process is accompanied by an appreciable increase in entropy resulting from extensive desolvation. This indicates inclusion of the fullerene balls in the calixarene baskets.[26] Practically no difference in the slopes and intercepts is observed between the complexes $C_{60} \cdot \mathbf{2}$ and $C_{70} \cdot \mathbf{2}$ but the difference between the intercepts for the complexes $C_{60} \cdot \mathbf{1}$ and $C_{70} \cdot \mathbf{1}$ is remarkable. This means that the extent of inclusion of C_{60} in the cavity of **1** is much higher than that of

For $C_{60} \cdot \mathbf{1}$:
$$T\Delta S_f^\circ = (1.5 \pm 0.2)\Delta H_f^\circ + (55.5 \pm 13.5);$$
$$\text{correlation coefficient} = 0.99 \quad (4a)$$

For $C_{60} \cdot \mathbf{2}$:
$$T\Delta S_f^\circ = (0.98 \pm 0.2)\Delta H_f^\circ + (18.6 \pm 10.9);$$
$$\text{correlation coefficient} = 0.98 \quad (4b)$$

For $C_{70} \cdot \mathbf{1}$:
$$T\Delta S_f^\circ = (1.0 \pm 0.03)\Delta H_f^\circ + (19.6 \pm 3.8);$$
$$\text{correlation coefficient} = 0.99 \quad (4c)$$

For $C_{70} \cdot \mathbf{2}$:
$$T\Delta S_f^\circ = (1.0 \pm 0.06)\Delta H_f^\circ + (21.9 \pm 4.7);$$
$$\text{correlation coefficient} = 0.99 \quad (4d)$$

C_{70}. This observation is in conformity with the fact[4,11] that p-$tert$-butylcalix[8]arene selectively sequesters C_{60} from a mixture of C_{60} and C_{70}. In CCl$_4$ medium at any temperature, the formation constant is found to be in the order $C_{60} \cdot \mathbf{3} > C_{60} \cdot \mathbf{1} > C_{60} \cdot \mathbf{2}$. The relatively high K in the case of the $C_{60} \cdot \mathbf{3}$ complex may be accounted for by the fact that the –OH groups bring about a large extent of 'preorganisation' of the host calixarene making a cone conformation through intramolecular H-bonding at the lower rim and causing the upper rim to open up. The C_{60} ball enters through the wider rim. This type of conformational preorganisation through H-bonding is not possible with the permethylated calix[6]arene (**2**), and this is responsible for the relatively low formation constant of its complex with C_{60}.

4 Conclusion

Both [60]- and [70]fullerene form 1 : 1 inclusion complexes with **1**, **2** and **3** in solution as shown by isosbestic points in toluene and o-xylene. The calixarene **2** in particular forms a stronger inclusion complex with C_{60} than with C_{70} as revealed by higher formation constants and larger extent of desolvation (intercept of $T\Delta S_f^\circ$ vs. ΔH_f° plot). The complexes also exhibit CT bands, the absorption maxima being consistent with Mulliken's

theory[21] and this correlation provides vertical ionisation potentials (I_D^v) of the calixarenes in solution. We believe that this is the first report on the determination of I_D^v of the calixarenes from CT transition energies of their complexes.

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