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Electron Donor-Acceptor Complexes of the Fullerenes C_{60} and C_{70} with Amines

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Based on electronic absorption spectroscopy, C_{60} is found to form complexes with aromatic amines with an enthalpy of association in the range 9-16 kJ mol^{-1}. Interaction of C_{70} with the amines is negligible. Cyclic voltammetric measurements confirm these observations.

Buckminsterfullerene, C_{60}, is known to have a high electron affinity[1)] and to readily form anions.[2)] In the solution phase, C_{60} seems to act as an electron acceptor with electron donors such as aromatic amines.[3-5)] Although electronic absorption spectra indicate the formation of ground-state electron donor-acceptor complexes of C_{60} with aromatic amines, there is some uncertainity with regard to quantitative aspects of complex formation. Thus, there are significant differences in the reported values of the equilibrium constants (0.047 M^{-1} and 0.18 M^{-1} respectively with dimethylaniline[3)] and diethylaniline[4)] respectively at room temperature). Furthermore, there is no estimate of the enthalpy of formation of these complexes. Since the enthalpy of formation directly gives the strength of donor-acceptor interaction, it is vitally important to determine this quantity. Another aspect of interest is the relative electron-accepting capabilities of C_{60} and C_{70}. In the literature, the equilibrium constant for the interaction of C_{70} with diethylaniline is reported to be[4)] higher (0.4 M^{-1}) than for C_{60} (0.18 M^{-1}), although there are indications to the contrary.[5)] We have therefore quantitatively studied the donor-acceptor interaction of C_{60} and C_{70} with dimethylaniline (DMA) and diphenylamine (DPA) in toluene solution by employing electronic absorption spectroscopy. We have also employed cyclic voltammetry to examine the interaction.

C_{60} and C_{70} were prepared and purified as reported elsewhere.[6)] The purity of the samples was verified by UV-visible as well as IR spectroscopy. The solvents used in this study were purified by distillation, followed by passing through alumina columns. Commercial diphenylamine (Riedel, Hannover) and dimethylaniline (BDH, India) were used after suitable purification. UV/Vis spectra were recorded with a Pye-Unicam instrument. Cyclic Voltammetry was performed using a BAS electrochemical analyser with gold electrodes and t-butylammonium perchlorate as the supporting electrolyte.

In Fig. 1, we show the absorption spectra of C_{60} solutions in toluene in the 400-700 nm region in the presence of varying concentrations of the amine donors. With increasing donor concentration, we see an accompanying increase in the absorbance, the change in absorbance with DMA being greater than with DPA. In both the cases, there is a slight blue-shift of the C_{60} bands, with the intensity of the 520 nm feature growing markedly. Although there is no distinct charge-transfer band, the changes in Fig. 1 are indicative of donor-acceptor interaction. We have obtained the equilibrium constants, K, from the absorbance data by employing the Benesi-Hildebrand (B-H) equation. Typical B-H plots for C_{60} with DMA and DPA are shown in

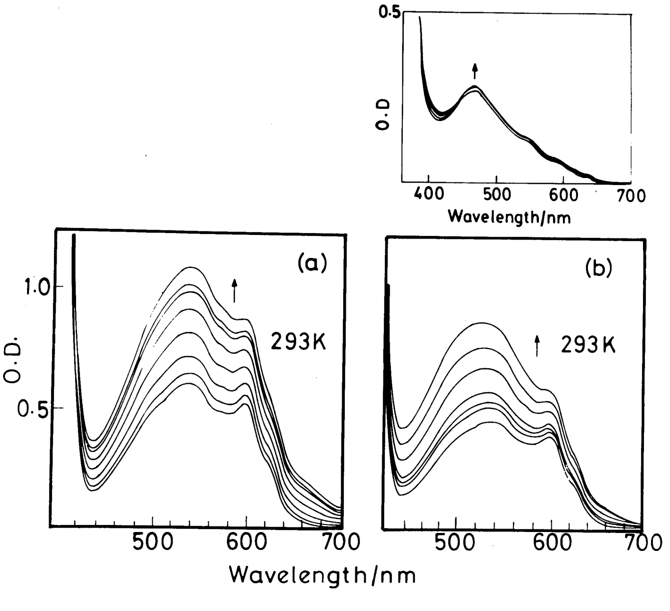

Fig. 1. (a) Absorption spectrum of C_{60} (6×10^{-4} M, toluene, 1cm cells) in the presence of 0, 0.38, 0.45, 0.53, 0.61, 0.68, 0.76, 0.84 M of DMA (from bottom to top curve). (b) Absorption spectrum of C_{60} (4.2×10^{-4} M, toluene, 1cm cells) in the presence of 0, 0.2, 0.25, 0.3, 0.5, 0.7, 1.0 M of DPA (from bottom to top curve). Inset shows the absorption spectrum of C_{70} (4×10^{-5} M, toluene, 1cm cells) in the presence of 0, 0.38, 0.53, 0.68, 0.84 M of DMA). Arrows show direction of increasing amine concentration.

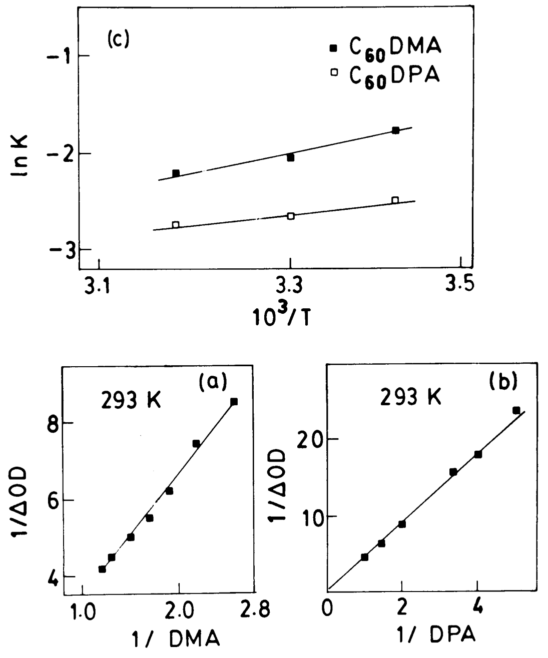

Fig. 2. Benesi-Hildebrand plots for (a) C_{60}-DMA and (b) C_{60}-DPA donor-acceptor complex formation in toluene in 293 K (c) lnK vs. 1/T plot for the two systems.

Fig. 2. The K values at 293 K are 0.2 M^{-1} and 0.08 M^{-1} respectively with DMA and DPA. Clearly, DMA is a better donor as expected based on its lower oxidation potential.

Based on variable temperature measurements (Fig. 2), we have obtained ΔH values for the formation of the D-A complexes. For C_{60}-DMA, the value is -16.5 kJ mol^{-1} and for C_{60}-DPA, it is -9.0 kJ mol^{-1}. In Table 1, we summarize the relevant data of the complexes of C_{60} studied by us. It is interesting that magnitude of ΔH as well as K decrease with increasing oxidation potential of the amine. The ΔH for the C_{60} + DMA complex is in

Table 1. Characteristics of amine complexes of C_{60}

Donor	E° (*vs.* Ag/AgCl)[a]	K/M^{-1} (293 K)[b]	ε_{CT}/M^{-1} cm^{-1} (520 nm)	ΔH/kJ mol^{-1}
DMA	0.854	0.20	9 x 10^3	-16.5
DPA	0.894	0.08	1.8 x 10^4	-9.0

a) In CH_2Cl_2 solution. b) In toluene solution.

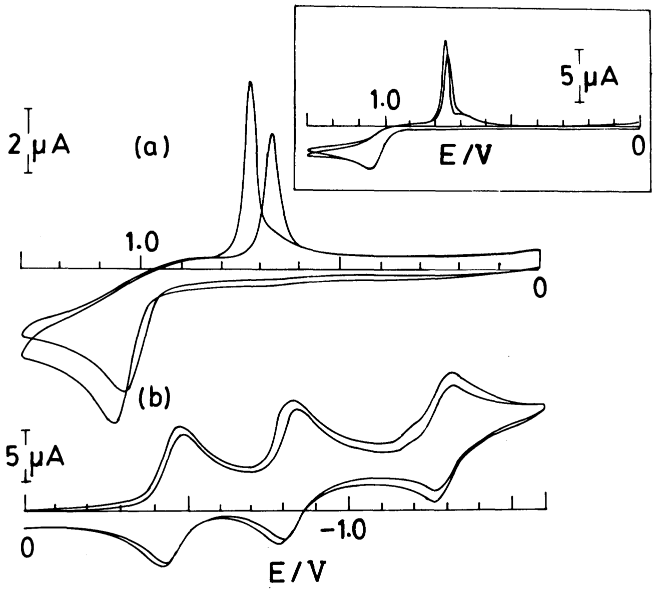

Fig. 3. (a) Oxidation of (1) DMA and (2) DMA in presence of C_{60} in CH_2Cl_2 solution; (b) Reduction of (1) C_{60} and (2) C_{60} in presence of DMA in CH_2Cl_2 solution. Inset shows the oxidation of (1) DMA and (2) DMA in the presence of C_{70}.

the range expected of weak π-π or π-σ donor-acceptor complexes.[7]

We have carried out similar spectroscopic studies of the interaction of C_{70} with DMA and DPA and find the changes in absorbance with increasing amine concentration to be marginal (see inset of Fig. 1). It seems that C_{70} does not form ground-state donor-acceptor complexes with amines in any meaningful concentration. Because of the very small changes, we were unable to obtain thermodynamic quantities for C_{70}-amine complexes. Clearly the electronic structure and properties of C_{70} are significantly different from those of C_{60}, as indeed pointed out by Kim et al.[8]

We have examined the formation of complexes of C_{60} and C_{70} with DMA and DPA by employing cyclic voltammetry in dichloromethane solution. In Fig. 3 we show the oxidation of DMA in CH_2Cl_2 solution (at 0.854 V). Addition of a small amount of C_{60} shifts this potential to 0.890 V. Similarly, the oxidation potential of DPA is shifted to a higher value on addition of C_{60}, indicating some charge-transfer from the amine to C_{60}, making the oxidation more unfavourable. The first two reduction potentials of C_{60}(-0.464 V and -0.856 V *vs.* Ag/AgCl), shift to a small extent on the addition of the amine. As an inset to Fig. 3, we show the oxidation of DMA in the presence of C_{70}. C_{70} causes only a marginal shift in the oxidation potential of DMA, supporting the conclusion from our spectroscopic studies that the interaction of C_{70} with amines is not as significant as with C_{60}.

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