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**Charge Transfer Complexations of C₆₀ with Substituted
Anilines and Aromatics**

**A Thesis
Presented to
The Faculty of the Department of Chemical and Materials Engineering
San José State University**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

**By
Robert Lee Campbell, Jr.
December 1999**

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Charge Transfer Complexations of C₆₀ with Substituted Anilines and Aromatics

Abstract

The charge-transfer complexes of C₆₀/substituted anilines and C₆₀/condensed aromatic hydrocarbons were identified and analyzed using uv-vis electronic absorption spectroscopy. The aromatic amines used were aniline, 2,6-dimethylaniline, N,N-diethylaniline, N,N-dimethylaniline, and N-methylaniline. The charge transfer interactions of these compounds with C₆₀ were studied in solvent solutions of dichloromethane and toluene at 25°C. The condensed aromatics used were naphthalene, phenanthrene, and pyrene. Their charge transfer interactions with C₆₀ were studied in toluene solvent solutions at temperatures between 15 and 40°C.

Using the Benesi-Hildebrand analysis, the equilibrium constants (K) were determined for C₆₀ charge-transfers interactions. For the C₆₀/aniline interaction, $K=0.28 \pm 0.04$. For the interaction of C₆₀/ aromatic hydrocarbons, the K values are as follows: C₆₀/naphthalene $K=0.08 \pm 0.015$, C₆₀/ phenanthrene $K=0.30 \pm 0.05$, C₆₀/pyrene $K=1.1 \pm 0.2$.

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1. Introduction

1.1 Background

It was long believed that pure carbon existed in only two allotropic forms at ambient conditions: graphite and diamond. With the discovery of a family of closed-cage carbon molecules, a third form of pure carbon was found to exist. The existence of these forms of carbon molecules was first suggested in 1970 by Osawa.^(1,2) Yet, It was not until 1985 that Smalley, Curl, and Kroto, observed these molecules in gaseous form.⁽³⁾ The infrared and mass spectral data showed carbon clusters consisting of 60, 70, 84, and higher carbon atoms were present. Their later work identified the 60 carbon molecule as having an icosahedral symmetry. Because this molecule resembled a geodesic dome, it was given the name "buckminsterfullerene" in honor the geodesic dome inventor Robert Buckminster Fuller. For this family of C_n cage molecules, the general name is "fullerenes". Later work by Kratschmer and coworkers in 1990, led to the development of a technique to produce condensed fullerenes.⁽⁴⁾

The C_{60} molecule is shown in Figure 1. This molecule is composed of twenty hexagonal rings of carbon. The electrons of these carbon rings are of sp^2 or p valance. The average C-C bond length in the C_{60} molecule is approximately 1.44 Å.⁽¹⁾ The binding energy per atom is 7.40 eV.⁽¹⁾ The curvature of the molecule is due the formation of the twelve pentagons from the arrangement of the hexagonal rings.⁽¹⁾ This arrangement gives the molecule an icosahedral (I_h) symmetry. The overall diameter of the C_{60} molecule is estimated to be 6.83 Å.⁽¹⁾

Unlike C_{60} , C_{70} (Figure 2) has a rugby ball shape. This shape results

Figure 1. The C_{60} or buckminsterfullerene molecule ⁽¹⁾

Figure 2. The C_{70} molecule ⁽¹⁾

from an additional ten carbon atoms around the midsection of the C₆₀ molecule. These additional atoms give this molecule the lower D_{5h} symmetry⁽¹⁾, a symmetry corresponding to a molecule that does not have an inversion center.

The differences in the number of carbon atoms and molecular symmetries give each fullerene molecule a unique spectrum. For example, the infrared spectrum reported for C₆₀ includes four prominent infrared lines: 527, 577, 1183, and 1428 cm⁻¹. Since C₇₀ has a lower symmetry, its infrared lines are 458, 535, 578, 674, 796, and 1431 cm⁻¹. Along with symmetry differences, the additional carbon atoms decrease the gap between the HOMO (highest unoccupied molecular orbital) and the LUMO the (lowest occupied molecular orbital).⁽⁵⁾ These effects are observed as a red shift of the absorption spectra of the fullerenes as shown in the C₆₀ and C₇₀ spectra in Figure 3. The features that are observed in each respective spectrum provide an unambiguous method of distinguishing the fullerene species and detecting impurities in the fullerene samples.⁽⁶⁾ The electronic absorption spectrum of C₆₀ exhibits strong peaks at 213, 257, and 329 nm and weak broad absorption from 450 to 600 nm. The spectrum of C₇₀ has strong peaks at 214, 236, 331, 360, 378, and 468 nm.⁽⁵⁾ Qualitatively, pure solutions of the various fullerene molecules exhibit a wide range of colors. Solutions of C₆₀ are deep purple, C₇₀ solutions are wine red colored, and higher fullerenes exhibit yellow to greenish colors.⁽⁵⁾ The colors exhibited by these solutions are very intense at very low concentrations (10⁻⁷ to 10⁻³ molarity).

Figure 3. The uv-vis electronic absorption spectra of pure C₆₀ (bottom) and C₇₀ (top) samples dissolved in toluene solvent. These spectra illustrate absorbance differences that can be used to identify and determine the purity of the samples.

Since their discovery, the fullerenes have attracted considerable attention. Materials scientists, chemists, and solid state physicists have suggested that solids made using fullerenes can be doped with atoms or molecules. These solids can become electron-conducting. Fullerene solids that have been doped with alkali metals, such as potassium or rubidium, have been shown to be superconductive at temperatures greater than 18 K. Another group of fullerene based electronically conductive materials are those resulting from the interaction of one or more fullerene molecules with one or more nucleophilic molecules.

Not only are these materials investigated for their electronic conductivity, they are also of interest because of their optical properties. When fullerenes are reacted with a molecule or an atom, the symmetry of the fullerene decreases. This symmetry decrease results in a material with nonlinear optical properties. Materials of this type emit light of a second frequency when exposed to light of an initial frequency. It is proposed that these fullerene-based materials may prove to be valuable as switches for optical applications.

Fullerenes have been studied using various techniques. Its solids and liquid solutions have been studied. Studies of current research interest are those that involve altering the fullerene's electronic orbitals by the addition of electrons. One way this can be done is by using molecular species that donate electrons to fullerenes, forming a charge transfer complex.

1.2 Fullerene Synthesis

The fullerene quantities necessary for various experimental and technological applications are produced by the contact arc technique. This method was developed by the Kratschmer group. The contact arc method involves passing a high current, 100 to 200 A, between graphite electrodes in an oxygen free chamber consisting of 200 Torr of He.⁽⁴⁾ The resulting heat vaporizes the rods creating a condensed discharge that consists of soot and fullerenes. The fullerenes in the discharge consist of C₆₀ (~13%), C₇₀ (~2%), and other higher fullerene molecules.⁽¹⁾ These quantities depend on the production conditions.^(1,4)

Although fullerenes are insoluble in most polar solvents such as water and alcohols, they are soluble in most non-polar aromatic solvents such as toluene and benzene. For separating the fullerenes from the rest of the soot, the discharge is treated with toluene, and the fullerenes are separated by continuous (Soxhlet) extraction.⁽¹⁾ The toluene-fullerene extract is then evaporated to dryness leaving behind a black solid, which consist of fullerenes. This solid is washed with diethyl ether for the removal of any remaining hydrocarbon impurities. The C₆₀, C₇₀, and, higher fullerenes are separated by dissolving the solid in toluene. This crude fullerene solution is then loaded to the top an alumina column, whereby, separation is done chromatographically.⁽⁷⁾ The purity of the separated fullerenes can be determined by either atomic mass spectroscopy, NMR, HPLC, or electronic absorption spectroscopy.

2. Charge Transfer Compounds

2.1 Charge-Transfer Complexes

Charge transfer complexes are molecular complexes that originate from the transfer of one or more electrons between a donor molecule with a high-level HOMO and an acceptor molecule with a low-level LUMO.⁽⁸⁾ As shown in Figure 4, charge transfer complexation occurs when the electrons from the HOMO of a donor molecule are transferred to the LUMO of an acceptor molecule. These interactions are relatively weak in that the ΔH is usually small, often with a strong spectroscopic electron transition in the near uv to visible range that corresponds to an electron returning to the donor.⁽⁵⁾ For example, colorless solutions of TCNE (tetracyanoethylene) and benzene will form a yellow solution on mixing.

Acceptor and donor species can be either organic or inorganic molecules. For this study, only organic species were considered. Donor species can be grouped into two categories. The first group of donors are those in which the available electrons are those from the π -orbital within a π -bond.⁽⁹⁾ These donor species are called π -donors. Examples of these donor molecules include benzene and other aromatic hydrocarbons. The second group of electron donors are those in which the electrons come from an molecule's available electrons.⁽⁹⁾ Examples of these include alcohols, amines, and organic sulfides.

Acceptor species have lower ionization potentials than donor species.⁽⁹⁾ Like donor species, there are several categories of acceptor species. These groupings include σ , ν (valance), and π -acceptors. The acceptor species of

Figure 4. Schematic of charge transfer complexation.

importance for complexes with molecular acceptor species are σ and π -acceptors because these species accept electrons into orbitals of their respective bonds. An example of a σ -acceptor is iodine while an example a π -acceptor is TCNE (tetracyanoethylene). The benzene/TCNE charge transfer complex is an example of a π - π donor-acceptor complex, where the electrons from the π -orbitals of the benzene molecule are donated to the π -orbitals of the TCNE molecule.⁽⁸⁾

Knowledge of charge-transfer complexation is not new. Examples of charge transfer complexes include dyes and indicators. It is only over the last thirty-five years that researchers have created solid charge transfer compounds. The first of these compounds used to make solid charge transfer complex is TCNQ (7,7,8,8-tetracyano-p-quinomethane). Studies have shown that the perchlorate salts of these compounds are electrically conductive at 54 K.⁽¹⁰⁾ Because of this, these solids are sometimes identified as organic metals. Another important compound is TMTSF (tetramethyltetraselenafulvalene). These compounds are of significance because its perchlorate salts have been found to exhibit semiconductive properties.⁽¹⁰⁾

The current interest in C_{60} is due to its physical properties. The band gap energy of C_{60} is 1.7 eV.⁽¹⁾ This band gap energy is very similar to that of 1.11 eV for silicon ⁽¹⁾ and consistent with known organic acceptors compounds. Because C_{60} is reactive, it is believed that a solid using these molecules can absorb hydrogen atoms without disrupting the overall fullerene structure.⁽¹¹⁾ It has also been suggested that fullerenes are better storage mediums for hydrogen than metal hydrides.⁽¹¹⁾ Studies of C_{60} doped with alkali metals

have catalytic properties similar to platinum.⁽¹¹⁾ Potassium doped C₆₀ have shown superconductivity within the temperature range of 18 to 33 K.⁽¹⁾ Compounds of C₆₀ and TDAE (tetrakisdimethylaminoethylene) have been found to be diamagnetic at 20 K.⁽¹²⁾ With the discovery of a diamagnetic C₆₀ compound, it believed that these charge transfer compounds are also superconductive.

2.2 C₆₀ Charge Transfer Materials

It has been proposed that fullerene charge transfer materials can be created by reacting fullerenes with appropriate electron donating molecules. Because the fullerenes C₆₀ and C₇₀ have similar reduction potential (-0.44 and -0.41 V, respectively)⁽¹³⁾ and an electron affinity of 2.65 eV⁽¹⁾, both molecules are considered as electron acceptors towards molecules of lower electron affinity. For C₆₀, it has been shown that it can accept up to six electrons while C₇₀ can accept up to four electrons.⁽¹⁾ It is also known to be very reactive. Based on these characteristics, the fullerenes are considered as excellent candidates for the formation of charge-transfer complexes.

Fullerenes have been reacted with a variety of organic and inorganic compounds. One group of donating compounds that complexes with C₆₀ are the amines. These compounds are classified as n-donors because of the lone pair of electrons on the nitrogen atom. These compounds have been widely studied because they are known to easily donate electrons to various acceptor compounds. C₆₀ has been reacted with various amines including diethylamine and trimethylamine. Another group of amines that the fullerenes have been

shown to complex with are the anilines. These compounds are characterized by having a benzene ring directly bound to the nitrogen. Figure 5 shows a few aniline group molecules.

Fullerene/amine charge transfer complexes have been characterized by various techniques. The most commonly used techniques are electronic absorption and emission spectroscopies. In a study by Wang⁽¹³⁾, the electronic spectra of fullerene/diethylaniline (DEA) complexes were studied. This study shows that the electronic absorption amplitude of C_{60} in a methylcyclohexane solvent increases upon addition of DEA. Along with this increase of absorption, a new absorption peak was observed at longer wavelengths. Wang suggested that this new peak may indicate the formation of the charge transfer complex, C_{60} /DEA, in the ground state.

The Rao group also studied fullerene complexation by electronic spectroscopy.^(14,15,16) Unlike Wang, they did not find any evidence for ground state interaction of C_{60} with aniline. They claimed that any observable interactions were due to exciplex formation. The exciplex that Rao claimed is a charge transfer complex that occurs when electrons are excited to higher electron state. Our group (Sibley, et al.) resolved this difference by showing that the interaction between C_{60} and aniline formed a charge transfer complex.⁽¹⁷⁾ We also showed that the energy of the maximum absorbance of the charge transfer spectra increases with increasing ionization potential energy of the substituted aniline.⁽¹⁷⁾ This study further shows that our charge transfer spectra we observed is real and that the energy of the charge transfer band is donor dependent.⁽¹⁷⁾

Aniline

N-methylaniline

2,6 dimethylaniline

o-toluidine

N,N dimethylaniline

N,N diethylaniline

Figure 5. Representative aniline compounds.

Further studies by the Sibley and the Francis groups show the absorption spectra of C_{60} is influenced by the solvent environment.⁽¹⁸⁾ Using C_{70} , Francis, et al. observed large solvent dependent changes in its phosphorescence spectrum.⁽¹⁸⁾ The Rao group extended their aniline studies to include the interaction of solvents with C_{60} . For this study Rao, et al. examined the ultraviolet-visible absorption spectra of C_{60} with benzene in a cyclohexane solvent.⁽¹⁶⁾ The results of this study indicate that C_{60} interacts with most aromatic solvents as well as the usual interaction between it and the amine donor species. This study by Rao, et al indicated the interactions between the π -orbitals of C_{60} and those of benzene and other aromatic compounds. A similar study by Ogilby and Shrolock shows that the spectra of solutions of C_{60} with substituted naphthalenes give rise to charge transfer bands.⁽¹⁹⁾ We observed C_{60} charge transfer complexation with a series of non-substituted condensed polyaromatic donor molecules.⁽²⁰⁾ These molecules are shown in Figure 6. From this study we determined the extent of binding and of complexation of fullerene/ π -donor systems.

Other studies have centered on the preparation of fullerene/amine solids. The Rao group prepared C_{60} /amine solids by reacting a C_{60} with methylamine.⁽²¹⁾ This solid exhibited a fluorescence peak at 326 nm at an excitation wavelength of 290 nm. Interestingly, the Pradeep group⁽²²⁾ reports the making of stable solid state charge transfer-complex by reacting C_{60} with hexamethylenetetrafulvalene (HMTTEF). Their results were confirmed by x-ray diffraction and infrared spectroscopy. Their spectra show a small peak shift of approximately 4 cm^{-1} , indicating a complex with a small amount of charge transfer.

naphthalene

phenanthrene

pyrene

Figure 6. Representative condensed aromatic hydrocarbons.

3. Experimental

3.1 Reagents and Specimen Preparations

Pure commercially purchased C₆₀ (Term Limited, 99.9%) was used for this study. The fullerene powder was stored in a vacuum dessicator between uses to minimized oxygen exposure. The anilines and condensed aromatic hydrocarbons were purchased. The anilines used for this study included aniline (Aldrich, 99%), 2,6-dimethylaniline (Aldrich, 99%), N,N-diethylaniline (Aldrich, 99%), N,N-dimethylaniline (Aldrich, 99%), and N-methylaniline (Aldrich, 99%). These anilines were further purified by passing them through columns of neutral alumina. The aromatics used included naphthalene (Aldrich, 99+%), phenanthrene (Aldrich, 98%), and pyrene (Aldrich, 99%). These compounds were used as received from the distributor.

The studies of the interaction between the fullerenes and substituted anilines were conducted in solvents of toluene (EM Science, spectroscopic grade > 99.9%) and dichloromethane (EM Science, HPLC grade > 99.9%). These solvents were commercially purchased and used as received from the distributor.

All test solutions were prepared from stock solutions of fullerenes. The stock solutions were then sealed to prevent evaporation and contamination. The solutions were also stored in the dark to prevent any photoreactions. For the fullerene/aromatic anime studies, the concentrations of the fullerene in solution were calculated from the mass of the fullerene dissolved in the solvent. The concentrations of the amine were calculated from its density and the

volume used for the specimen. For the charge transfer studies using electronic absorption, the concentrations of the fullerene stock solutions were determined spectroscopically at 25°C using extinction coefficient values determined by Thomas.⁽⁶⁾ The polyaromatic solutions that were used for the electronic absorption studies were prepared by dissolving the respective polyaromatic solid using toluene. The concentrations of these stock solutions were determined by weighing the C₆₀ solid before dissolving and filling to volume with require solvent. For the FTIR studies, mulls were prepared by grinding 5 to 10 mg of fullerene with a slight excess of liquid aniline. After grinding, the mulls were mounted between KBr plates.

3.2 Equipment and Methods

Data for the determination of the equilibrium constants were recorded using either a Cary 3 double beam spectrophotometer or a Hewlett-Packard 84542A uv-vis diode array spectrophotometer. Both spectrophotometers have temperature controllers. Before measurements, the solutions remained at the required temperature for ten minutes to allow for thermal equilibrium. All spectral measurements were taken using matched quartz cuvettes (path length, 1 cm) against a corresponding donor species to correct for variation in the dielectric constants of the solutions. After filling, the cells were capped to prevent of the evaporation of the solvent. Since the aniline compounds are known to decompose, all fullerene/substituted aniline solutions were prepared and studied within a two hour time period. This time period was not necessary for the spectral studies of the polyaromatics.

The C₆₀/substituted aniline solid infrared spectra were recorded using a

Perkin-Elmer model 1800 FTIR spectrometer. All mulls were studied in a nitrogen atmosphere. After each study the KBr plates were cleaned with either ethanol or methanol. The plates were stored in a dessicator.

3.3 Stability Constant Calculation

The interactions between C₆₀ and the donor species were observed as a new peak corresponding to the formation of the charge-transfer complex in the ground state or growth in the original absorption bands. The strength of this complex is directly related to the magnitude of the equilibrium constant, K. Equilibrium constants for the donor-acceptor interaction observed in this experiment were determined using the Benesi-Hildebrand analysis.⁽²³⁾ For this analysis it was assumed the C₆₀/donor interaction formed a 1:1 charge transfer complex. This analysis follows the interaction

where the complex, C, results from the interaction of the donor, D, and the acceptor, A. The resulting equilibrium constant is given by

$$K = \frac{[C]}{[D][A]} \quad (2.)$$

The total concentration of the donor and acceptor species in solution is given by $[D_T] = [D] + [C]$ and $[A_T] = [A] + [C]$. After substituting for [D] and [A] and inverting Equation 2

$$\frac{1}{K} = \frac{([D_T] - [C])([A_T] - [C])}{[C]}$$

$$= \left(\frac{[D_T] [A]}{[C]} - [D_T] \right) - [A_T] - [C] \quad (3.)$$

For this experiment, the concentration of the donor species was much greater than that of acceptor and complex. Under these conditions, Equation 3 now becomes

$$\frac{1}{K} = \left(\frac{[D_T] [A]}{[C]} - [D_T] \right) \quad (4.)$$

The absorbance, A , of the complex follows Beer's law,

$$A = \epsilon [C] l \quad (5.)$$

where ϵ is the extinction coefficient of the complex and l path length of the cell. Substituting the above equation into Equation 4 gives

$$\frac{1}{K} = \frac{[D_T] [A_T] \epsilon l}{A} - [D_T] \quad (6.)$$

After dividing this equation by $[D_T] \epsilon$ and rearranging, the following is obtained

$$\frac{[A_T] l}{A} = \frac{1}{K [D_T] \epsilon} + \frac{1}{\epsilon} \quad (7.)$$

Since the above equation is in $y=mx+b$ form (the equation of a line), the K is determined by dividing the intercept, $\frac{1}{\epsilon}$, by the slope of the line, $\frac{1}{K [D_T] \epsilon}$, from the plot of $\frac{[A_T] l}{A}$ vs $\frac{1}{[D_T]}$. These calculations were done using the linear regression package in the Microsoft Excel® computer spreadsheet program for either Apple Macintosh® computers or Microsoft DOS® compatible computers that uses Microsoft Windows®. The data are presented in Appendix 1.

4. Results and Discussion

4.1. C_{60} /Substituted Aniline Interactions

The studies of the interactions between C_{60} and aniline were carried out using a Hewlett-Packard spectrophotometer. Pure C_{60} in toluene solutions are purple. Upon the addition higher concentrations of aniline, the C_{60} in toluene solutions became brownish in color. This color change was not associated with any charge transfer complex formation. According to Catalán, et al., the observed color results from the difference in absorbance intensities of toluene, aniline, and C_{60} .⁽²⁴⁾

The interactions of C_{60} and the anilines were established in works by Rao, et al.^(14,15,16) and Wang.⁽¹³⁾ From both studies, the K values were determined by Benesi-Hildebrand analysis. In their studies, it was observed that the addition of aniline to C_{60} /toluene solution leads to increased absorbance, characteristic of donor-acceptor interaction. Results for a series of solutions of varying donor concentration at 20°C are shown in Figure 7. Overall, the intensity of C_{60} increases with increasing aniline concentration. This increased intensity is similar to those increases observed for other amine systems.

On the basis of the observed data, it was concluded that aniline interacts with C_{60} . Despite this interaction, the spectra in Figure 7, show no indication of charge transfer complex formation. Although there is no evidence of complexation observed in the spectra, it cannot be concluded that the charge transfer complex is absent. It is possible that more than one complex

Figure 7. Representative absorbance spectra of C_{60} (2×10^{-4} M) in toluene with addition of aniline. Aniline concentrations of 0, 0.5, 0.85, 1.0, 1.15, 1.5M are shown, with increasing concentrations from bottom to top.

species are present in the solution.⁽²⁵⁾ Species present may include C₆₀/aniline complexes before charge transfer and the C₆₀/aniline complexes after the transfer of the charge.

Changes in the spectra are noticeably larger in the region around 450nm. Unlike the spectra reported for similar C₆₀/amine systems, the change of the C₆₀ absorbance is largest in the shorter wavelength region.⁽¹³⁻¹⁶⁾ This point will be discussed later.

The equilibrium constants were determined from the concentration dependence of the spectral data by using the equation from the Benesi-Hildebrand analysis, Equation 7. For the use of this equation, it was assumed the resulting complexation was 1:1 ^(23,25) and the absorbance of the complex increases linearly with increasing donor concentration. The data were taken at 440nm, and results of the analysis are shown in Figure 8. Linear regression analysis of the plot leads to values of $K=0.28 \pm 0.04$, a result slightly larger than the value of 0.20M^{-1} reported by Seshadri, et al.⁽²¹⁾ for C₆₀/dimethylaniline in the same solvent. It is also higher than the result reported by Wang of $K=0.18 \pm 0.04$ for C₆₀/diethylaniline in benzene.⁽¹³⁾

Based on its higher ionization potential, aniline should be a poor donor. ⁽²⁶⁾ But, the larger magnitudes of the observed stability constants of the C₆₀/diethylaniline and C₆₀/dimethylaniline interactions may suggest the importance of steric effects on complexation in solution.

As shown in Figure 7, the relative increase in absorbance upon addition of aniline is largest in the lower wavelength region. For a series of related donors with a single acceptor, the peak maximum of a charge-transfer band is

Figure 8. Benesi-Hildebrand plot for complexation of C_{60} /aniline in toluene.

approximately given by:

$$h\nu_{CT} = IP - C_1 + C_2/(IP-C_1) \quad (8.)$$

where C_1 and C_2 are constants for a given acceptor ($C_1 \gg C_2$), and IP is the ionization potential of the donor.⁽²⁷⁾ Over small ranges, a plot of $h\nu_{CT}$ versus IP should be roughly linear, with

$$h\nu_{CT} = IP - \text{Constant} \quad (9.)$$

This behavior has been empirically observed for iodine and other acceptor molecules.⁽²⁸⁾ To investigate the behavior of C_{60} , uv-vis spectra were recorded for C_{60} in dichloromethane solutions with various anilines.

Dichloromethane, a non-aromatic solvent, is used to eliminate any possible solvent interactions with the C_{60} .⁽¹⁶⁾ This study was carried out on the Cary 3 spectrophotometer. The 25°C spectra, which were referenced against the appropriate amine solutions, were then subtracted from the spectrum of C_{60} in dichloromethane without the amine. This subtraction was done to eliminate the effects due to the solvent. The results are shown in Figure 9. Slight oscillations observed in the spectra were due to the baseline correction process and the low intensity of the C_{60} charge transfer bands. As can be seen in the plot, the maximas of the charge-transfer bands vary from 420nm for aniline to nearly 560 nm for DEA. The absorbance maxima of the charge transfer bands do not coincide with the maxima of the respective amine absorbances, and intensities of the charge transfer bands are sometimes larger than those of the amine solutions. These results are summarized in Table 1 against the

Figure 9. Charge-transfer bands for C₆₀ with various substituted anilines: (a) aniline, (b) o-toluidine, (c) 2,6-dimethylaniline, (d) N-methylaniline, (e) N,N-dimethylaniline, and (f) N,N-diethylaniline.

respective ionization potentials. The ionization potentials shown in the table are those reported by Maier and Turner.⁽²⁹⁾ unless otherwise noted. A plot of the λ_{max} of the charge transfer peak versus ionization potential is shown in Figure 10. The data are linear and in agreement with Equation 9 for the substituted anilines shown. Diphenylamine was not included since it did not fit the pattern, possibly due to different resonance interactions as a result of the additional benzene ring. The full width half maximum (FWHM) of the bands appears to increase slightly as the bands shift to lower energies, suggesting increased interactions with the donors of lowest ionization potential. It is clear from the results of this study that the observed changes in the C₆₀/substituted aniline spectra are indeed due to the presence of charge transfer absorptions. The position of the C₆₀/aniline donor-acceptor band (420 nm) is found to be at higher energy than predicted by recent theoretical calculations, which places it between 650 and 800 nm.⁽³⁰⁾ These results suggest that in spite of its large size and unique symmetry C₆₀ acts in a manner similar to that of other π -acceptors with regard to its donor-acceptor behavior in solution.

This study was extended to examine the solid state interactions of C₆₀/substituted aniline solids by FTIR spectroscopy. The resulting spectra of the C₆₀ interactions were measured in the presence of excess substituted aniline compounds. These spectra are shown in Figure 11. These spectra represent the vibration modes of the C₆₀/substituted aniline interaction referenced against the C₆₀ 576 cm⁻¹ vibration modes. Complex vibration modes were not observed because these modes have vibration frequencies below the cutoff frequencies of the KBr plates. The FTIR spectra of the C₆₀/substituted anilines were compared with the C₆₀ spectrum. From this

Table 1. Ionization Potentials and Charge-Transfer Band Maxima for C₆₀ with Substituted Anilines

Compound	Ionization Potential (eV)^a	C-T Peak Maximum (eV)
Aniline	8.1	2.95
o-Toluidine	7.83^b	2.82
2,6 dimethylaniline	7.75	2.71
N methylaniline	7.65	2.54
N,N dimethylaniline	7.45	2.46
N,N diethylaniline	7.2	2.21

a) Ionization values from Reference 29 unless otherwise noted.

b) Value from Reference 26.

Figure 10. Plot of energy of maximum absorbance of charge-transfer bands of C_{60} /aniline complexes versus ionization potentials of the respective anilines.

Figure 11. Overlay FTIR plots of C₆₀/anilines samples. From top to bottom: C₆₀/aniline, pure C₆₀, C₆₀/N,N-dimethylaniline, C₆₀/N,N-diethylaniline. Intensities are not normalized.

comparison at 576 cm^{-1} , evidence for C_{60} /amine interaction is observed. From these scans, it is observed that the C_{60} /amine peaks are shifted relative to the C_{60} peak. The C_{60}/N , N -dimethylaniline and C_{60}/N , N -diethylaniline peaks are blue shifted with respect to the C_{60} infrared peak. The C_{60} /aniline peak is red shifted with respect to the C_{60} peak. The observed blue shifts were unexpected. For π -systems such as C_{60} , the electron transfer to the antibonding LUMO of C_{60} would be predicted to cause red shifting due to the lowering of the force constant.

It has been reported that this behavior is observed in the Raman spectra of aromatic-nitro acceptor molecular complexes with dimethylaniline and diethylaniline.⁽³¹⁾ These complexes showed blue shifts in some NO_2 stretching vibrations up to 20 cm^{-1} . Given this, the blue shifts of the vibration modes of the acceptor C_{60} should be smaller due to the degree of electron delocalization and small extent of the donor amine interaction.

The observed infrared vibrational modes of the C_{60} /substituted aniline solid increase from C_{60} /aniline to C_{60} /diethylaniline. This shift indicates that the interaction strength increases. These results are consistent with the results expected on the basis of ionization potential. However, our infrared spectra solid results appear not to agree with the results obtained from the ultraviolet-visible absorption spectra in solution where solvent interactions could be of importance. It should also be pointed out that reproducible features are seen on the high frequency side of the blue shifted spectra. These features give these bands an asymmetric appearance. Based on the shapes and the shifts of the infrared spectral bands, the order of the solid state interactions is supported by these data.

4.2 C_{60} /Aromatic Hydrocarbon Interactions

As mentioned earlier, aromatic solvents have been shown to interact with C_{60} . The interaction of benzene with C_{60} was first shown by Rao, et al.⁽¹⁶⁾ From their studies, an equilibrium constant of 0.2 M^{-1} was determined for C_{60} /benzene in cyclohexane using similar analysis. In a study of the C_{60} /substituted naphthalenes interaction by Ogilby and Shurlock, charge transfer absorbances for C_{60} /methylnaphthalene in toluene were reported with an equilibrium constant of $K=0.8\pm0.2$.⁽¹⁹⁾ However, no studies have been done to quantify the interactions of C_{60} with non-substituted aromatic multi-ring aromatic hydrocarbons.

Figure 12 shows representative absorption spectra of C_{60} with increasing concentrations of naphthalene at 25°C . The increased absorbance in the region near 400-500 nm is characteristic of donor-acceptor interaction and is not due to naphthalene absorbance. All solutions were measured against naphthalene blanks to ensure correct absorbance values and to correct for changes in dielectric constant. The equilibrium constant was determined from the concentration dependence data by using the Benesi-Hildebrand equation.⁽²³⁾ These data were taken at 426 nm, near the absorbance maxima in order to minimize error. The resulting Benesi-Hildebrand plot is also shown in Figure 12. The K value of the C_{60} /naphthalene system at 25°C was determined by linear regression to be 0.080 ± 0.015 . This result agrees well with the value for C_{60} /methylnaphthalene complexation in toluene reported by Ogilby and Shurlock. Because of the weak nature of the interaction, a large number of data points were taken to ensure experimental

Figure 12. Top: Representative absorption spectra of C₆₀ (4.2×10^{-4} M) in toluene with successive amounts of naphthalene ranging from concentrations of 0.43 to 1.3 M. Increasing concentrations are shown from top to bottom. Bottom: Benesi-Hildebrand plot for C₆₀/naphthalene at 426 nm and 25°C.

accuracy. Similar Benesi-Hildebrand analyses were performed using phenanthrene and pyrene. The resulting spectra and plots are shown in Figures 13 and 14. At 25°C, C₆₀/phenanthrene complexation in toluene has a K=0.37±0.07 while that for C₆₀/pyrene in toluene has K=1.1±0.2. The equilibrium constant increases by an order of magnitude as the number of aromatic rings of the donor (and therefore the π - π^* interaction) increases from naphthalene to pyrene. The results suggest significant interactions of fullerenes with aromatic molecules such as those often used as solvents. It also suggests that the extent of binding should be even larger for larger polyaromatic hydrocarbon molecules such as coronene. These interactions may play a role in the spectral changes found for luminescence spectra of C₆₀ in aromatic solvents.

Similar measurements of C₆₀/naphthalene and C₆₀/phenanthrene solutions were made at various temperatures. For the C₆₀/naphthalene, the spectra were obtained at temperatures of 15, 25, 30, and 40°C. The spectra C₆₀/phenanthrene solutions were obtained at 20, 25, 30, and 35°C. Like their respective solutions at 25°C, the K values were determined by Benesi-Hildebrand analysis.

To calculate K at the temperatures as given in Table 2, the concentrations of the components were corrected for toluene solvent expansion by using the equation⁽³²⁾

$$v = v_{0^\circ\text{C}}(1 + 1.028 \times 10^{-3}t + 1.779 \times 10^{-6}t^2) \quad (10.)$$

Figure 13. Top: Representative absorption spectra of C_{60} ($4 \times 10^{-4}M$) in toluene with increasing phenanthrene concentrations bottom to top (0.35 to 1.08 M, respectively). Bottom: Benesi-Hildebrand plot for C_{60} /phenanthrene at 423 nm and 25°C.

Figure 14. Top: Absorption spectra of C_{60} (4×10^{-4} M) in toluene with increasing pyrene concentration bottom to top (0 to 0.22 M, respectively). Bottom: Benesi-Hildebrand plot for C_{60} /pyrene at 506 nm and 25°C. Bottom: Benesi-Hildebrand plot for C_{60} /pyrene at 506 nm and 25°C.

**Table 2. Equilibrium Values of Naphthalene and Phenanthrene
at Measured Temperatures.**

C₆₀/Naphthalene		C₆₀/Phenanthrene	
Temperature (°C)	K_{eq}	Temperature (°C)	K_{eq}
15	0.091±0.018	20	0.38±0.07
25	0.080±0.013	25	0.36±0.07
32	0.064±0.015	30	0.35±0.06
40	0.059±0.017	35	0.32±0.05

where v_0 is the initial volume of toluene at 25°C and t is the solvent's temperature in degrees Celsius. Once the concentrations are corrected for temperature, the K at each temperature was determined by linear regression. The K values for C_{60} and its respective donor species as shown in Table 2 decreases with increasing temperature. These data show that the charge transfer decreases with increasing temperature

Evaluation of the equilibrium constants at different temperatures allows for enthalpy determinations by a van't Hoff plot of $\ln K$ vs. $1/T$. However, the K 's for weak complexes are unreliable due to deviations from Beer's Law. Therefore, the values of K and ϵ are not as well defined as the combined product $K\epsilon$.^(27, 33, 34) The slope of the plot of $\ln K\epsilon$ versus $1/T$ is often used as a better method for enthalpy determinations in weak systems.⁽²⁷⁾ This requires that ϵ does not change with temperature, which is a valid assumption for most systems over such a small temperature range.⁽²⁷⁾ For example, when corrected for expansion of the solvent, we found the calculated ϵ for C_{60} to be unchanged within experimental error over the temperature range of study.

If ϵ is constant over a temperature range of less than 50°C, then the equations become

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11.)$$

$$\ln K\epsilon = \ln K + \ln \epsilon \quad (12.)$$

$$= -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \epsilon \quad (13.)$$

Provided that $\epsilon \approx 1$, equation 12 resembles 11. Therefore, a plot of $\ln K\epsilon$ versus $1/T$ is similar to the plot of $\ln k$ versus $1/T$. Thus the calculated enthalpy and entropy are independent of plotting method. Using the above equations, the ΔH and ΔS for complexation are determined from the slope and intercept of the linear plot. These values were calculated using the spreadsheet software package.

The errors of the $K\epsilon$ values are based on a linear regression of 95% confidence. $K\epsilon$ with an error less than 20% was considered as acceptable. This amount of error was much less than $K\epsilon$ reported other groups doing similar studies. The error of the ΔH and ΔS values was determined by half of the absolute difference of the maximum and minimum of the possible slopes of the error on the $K\epsilon$ values carries

Plots of $\ln K\epsilon$ versus $1/T$ for naphthalene and phenanthrene were made and are shown in Figures 15 and 16. The slope of the plots shows that the interaction of the donor-acceptor complex is temperature sensitive. As the temperature increases, the interaction strength of the complex decreases. An excellent linear fit to the data results in values of $\Delta H = -1.7 \pm 0.3$ kJ/mole for naphthalene and $\Delta H = -2.8 \pm 0.4$ kJ/mole for phenanthrene. This fit also gives values of $\Delta S = 49.6 \pm 1.1$ J/mole-K for naphthalene and $\Delta S = 54.8 \pm 1.7$ J/mole-K for phenanthrene. Although the larger enthalpy for the phenanthrene appears to be consistent with K in the C_{60} /phenanthrene system, it should not be concluded that the values for ΔH and K are directly related. The enthalpy values

Figure 15. $K\epsilon$ versus $1/T$ plot for naphthalene for the determination of ΔH° and ΔS° .

Figure 16. $K\varepsilon$ versus $1/T$ plot for C60/phenanthrene for the determination of ΔH° and ΔS° .

for C₆₀/polyaromatics are somewhat smaller than those reported than those reported for C₆₀/aniline complexation. However, they are of the size expected for weak π - π binding of this magnitude of K.⁽²⁵⁾

For a series of related donors with a single acceptor, the plot of the peak maximum $h\nu_{CT}$ of a charge-transfer band versus the ionization potential of the donor should be roughly linear. This behavior has been empirically observed for C₆₀ with substituted naphthalenes as well as with anilines.⁽³⁵⁾ To obtain the charge transfer bands, uv-vis spectra were recorded at room temperature for C₆₀ dissolved with various aromatic hydrocarbons in toluene. Anthracene was added to this study to determine if another condensed aromatic hydrocarbon follows the observed trend. All spectra were referenced against the appropriate aromatic hydrocarbon solutions and were then subtracted from the spectrum of C₆₀/toluene. These results are shown in Figure 17. The maximas of the charge transfer bands do not coincide with the maxima of the respective aromatic hydrocarbon absorbances. While the charge transfer band for pyrene and anthracene are smooth curves in the visible region, bands at higher energy show reproducible oscillations of about 3.1 eV. As has been noted, this structure is due to changes in the relatively large C₆₀ absorbances in the region.⁽³⁵⁾

The strong UV absorbances of C₆₀ makes baseline correction difficult, and results for charge transfer absorbances are only reliable above 390 nm. Because the charge transfer maxima for naphthalene and phenanthrene are obscured by the oscillations, the estimates of the charge transfer peak maxima for these compounds were based on their peak profiles. However the

data show, an overall increase of the charge transfer bands from naphthalene to anthracene. The charge transfer band data as summarized in Table 3 show that the charge transfer band maxima increase with the ionization energy of the aromatic species. This increase agrees with similar increases that were observed for aniline species. The FWHM of the bands in Figure 17 increases as the bands shift to lower energy, and is quite broad for pyrene. This behavior is consistent with a wider range of interactions with the donors of lowest ionization potential. This FWHM increase has also been observed for the complexation of C₆₀/aniline. As shown in Figure 18, the charge transfer maxima in the current study appear to fall on the same line as the charge transfer maxima of C₆₀/anilines. This trend does not necessarily imply π - π rather than n- π binding for the substituted aniline systems. To resolve this question, further studies using other techniques are required.

Figure 17. Charge transfer bands for C₆₀ complexes with a) naphthalene, b) phenanthrene, c) pyrene, and d) anthracene.

Table 3. Ionization Potentials and Charge-Transfer Band Maxima for C₆₀ with Aromatic Hydrocarbons

Compounds	Ionization Potential (eV)^a	C-T Peak Maximum (eV)
Naphthalene	8.14	2.99
Phenanthrene	7.86	2.98
Anthracene	7.45	2.52
Pyrene	7.41	2.45

a) Ionization values from Reference 36.

Figure 18. Plot of energy of maximum absorbance of charge-transfer bands of C_{60} /aromatic hydrocarbon complexes versus ionization potentials of the respective aromatic hydrocarbon.

Conclusions

The results show C₆₀ acceptors form ground state charge transfer complexes with aromatic amine donors. From ultraviolet-visible absorption spectra, the charge transfer maxima increase linearly with increasing ionization potential of the amines. Interestingly, this relationship was not observed for the infrared spectra of C₆₀/substituted aniline solids. The infrared spectra show shifts indicating complexation strengths of C₆₀/amine solid complexes increasing with decreasing ionization potential. These differences may indicate solvent/donor interactions.

The C₆₀/condensed aromatic hydrocarbon study supports the importance of solvent effects on the charge transfer complexation. This study shows the importance of π - π^* interactions in the complexation process. These interactions must also be considered when examining the acceptor/donor interaction of C₆₀ and aromatic amines. Because of these large transfer complexations, it cannot be concluded that electron donation is from the unbonded electrons from nitrogen atom of substituted anilines to C₆₀. Therefore, π - π^* interactions for aromatic amines must be must be considered.

6. References

1. M.S. Dresselhaus; Dresselhaus, G.; Eklund, P.C., J. Mater. Res., **8** (1993), 2045- 2093.
2. Istvan Hargittai, The Chemical Intelligencer, **1**, (1995), 6- 9.
3. H.W. Kroto; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E; Nature, **318** (1985), 162-163.
4. W. Krastschmer; Fostiropoulos, K; Huffman, D., Chem. Phys. Letters, **170** (1990), 167 - 170.
5. C.M. Lieber; Chen, C.C., "Preparation of Fullerenes" in Solid State Physics: Advances in Research and Applications, Vol. 48 H. Ennereich, F. Spaepen, Editors, Academic Press, San Deigo, CA (1994), 112-129.
6. R.N. Thomas, Anal. Chimica Acta, **289** (1994), 57- 67.
7. K. Jinno; Fukuoka, K.; Fezter, J.; Biggs, J.W., J. Microcolumn Separations, **5** (1993), 2.
8. N.S. Isaacs, Physical Organic Chemistry, Longman Scientific and Technical: New York (1987), 67-70.
9. F. Gutmann; Keyzer, H.; Lyons, E., Organic Semiconductors, Part B, R.E. Krieger (1983).
10. J.M. Williams, Organic Superconductors, Prentice Hall: Englewood Cliffs, New Jersey (1993).
11. "New Chemistry for Carbon", www.usfullerene.com.
12. K. Kikuchi; Kikuchi, M.; Namiki, T.; Saito, K.; Ikemoto, I.; Murata, K.; Ishiguro, T.; Kobayashi, K., Chem. Lett., (1987) 931.
13. Y. Wang, J. Phys. Chem., **92** (1992), 764-767.
14. R. Seshadri; Rao, C.N.R.; Pal, H; Mukherjee, T.; Mittal, J.P., Chem. Phys. Lett., **205** (1993), 395-398.

15. D. K. Palit; Ghosh, H.N.; Pal, H.; Sapre, A.V.; Mittal, J.P.; Seshadri, R.; Rao, C.N.R., Chem. Phys. Lett., **198** (1992), 113-117.
16. C.N.R. Rao; Seshadri, R.; Govindaraj, A.; Mittal, J.P.; Pal, H.; Mukherjee, T., J. Molecular Structure, **300** (1993), 289-301.
17. S.P. Sibley; Campbell, R.L.; Silber, H.B., J. Phys. Chemistry, **99** (1995), 5274.
18. S.P. Sibley; Campbell, R.L.; Nguyen, Y.; Silber, H.B.; Argentine, S.M.; Francis, A.H., "Effect of Solvent on the Photophysical Behavior of Fullerenes" in Proceedings of the Symposium on Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Fullerenes Group, Vol. 95-10, Editors: R.S. Ruoff, K.M. Kadish, The Electrochemical Society, Pennington N.J. (1996), 406 - 413.
19. P.R. Ogilby; Shurlock, R.D., J. Photochem. and Photobio. A, **91** (1995),
20. S.P. Sibley; Nguyen, Y.; Campbell, R.L.; Silber, H.B., Spectrochimica Acta Part A **53** (1997), 679 - 684.
21. R. Seshadri; D' Souza, F.; Krishnan, V.; Rao, C.N.R. Chem. Lett. (1993), 217-220.
22. T. Pradeep; Singh, K.K.; Sinha, A.P.B.; Morris, D.E., J. Chem. Soc., Chemical Communications, (1992), 1747.
23. H.A. Benesi; Hildebrand, J.H.; J. Phys. Chem., **71** (1949), 2703-2707.
24. J. Catalán; Saiz, J.L.; Laynez, J.L.; Jagerovic, N.; Elguero, J., Angew. Chem. Int. Ed. Engl., **34** (1995), 105-107.
25. K.A. Connors, Binding Constants: The Measurement of Molecular Complex Stability, Wiley: New York, (1987).
26. T. Kobayashi; Nagakura, S., Bull. Chem Soc. Japan, **47** (1974), 2565.
27. R.S. Mulliken; Person, W.B., Molecular Complexes, Wiley-Interscience: New York, (1969) 419-427.
28. H. Mc Connell; Ham, J.S.; Platt, J. R., J. Chem. Phys., **21** (1953), 66.
29. J.P. Maier; Turner, D.W., J. Chem. Soc., Faraday Trans. 2, **69** (1973), 521-524.

30. J. Li; Feng, J.; Sun, C., J. Phys. Chemistry, **98** (1994), 8636.
31. A.M. Hindaway; Nassar, A.M.G.; Issa, R.M.; Issa, Y.M. Indian J. Chem., **8** (1993), 2068.
32. J.A. Dean, editor, Lange's Handbook of Chemistry, 13th Edition, McGraw-Hill: New York (1985), 10-129.
33. R. Foster, Organic Charge-Transfer Complexes, Academic Press: New York (1969).
34. P.H. Emile; Foster, R., Tetrahedron, **21** (1965), 2851-2855.
35. S.M. Argentine; Francis, A.H., Mat. Res. Soc. Symp. Proc., **359** (1995), 221.
36. D. Lide, editor, Handbook of Chemsitry and Physics, 76th edition 1995-1996, CRC Press: Boca Raton, FL, 10-227, 10-228.

Appendix I.
Data for C₆₀ Charge Transfer Complexation with
Anilines and Condensed Aromatic Hydrocarbons

Appendix A-1
Uv-vis Spectrophotometric Data for C₆₀/Aniline

Wavelength	0 M Aniline	0.5 M Aniline	0.85 M Aniline	1.0 M Aniline	1.15 M Aniline	1.5M Aniline
402	0.54799	0.60826	0.62636	0.63486	0.64854	0.68141
406	0.54381	0.6058	0.62447	0.63263	0.6465	0.6792
410	0.4882	0.54947	0.56863	0.57713	0.59157	0.6231
414	0.29967	0.36337	0.38701	0.39821	0.41408	0.44557
418	0.17831	0.24301	0.26776	0.27959	0.29651	0.32654
422	0.1133	0.17651	0.20415	0.21703	0.233	0.26459
426	0.06711	0.13419	0.16183	0.17485	0.19299	0.22296
430	0.04576	0.11194	0.14362	0.15775	0.17416	0.20726
434	0.03734	0.10532	0.1362	0.14996	0.16753	0.19914
438	0.0343	0.10307	0.13376	0.14772	0.16563	0.19702
442	0.03622	0.10477	0.13623	0.15028	0.16788	0.19954
446	0.04044	0.10928	0.1402	0.15405	0.17183	0.20288
450	0.04564	0.11429	0.14452	0.15796	0.1759	0.20642
454	0.0515	0.11943	0.14886	0.16206	0.1799	0.20955
458	0.05728	0.12288	0.15352	0.16669	0.18317	0.2137
462	0.06367	0.12895	0.15707	0.16969	0.18665	0.21526
466	0.0697	0.13235	0.16112	0.1738	0.18927	0.21844
470	0.07721	0.13918	0.1646	0.17601	0.19273	0.21857
474	0.08437	0.14342	0.16887	0.17992	0.19522	0.22142
478	0.09242	0.1485	0.17299	0.18391	0.19814	0.22354
482	0.10016	0.15201	0.17744	0.18906	0.201	0.22504
486	0.10646	0.1554	0.18356	0.19206	0.202	0.22775
490	0.11569	0.16177	0.18433	0.1932	0.20393	0.22934
494	0.12227	0.16772	0.18561	0.19383	0.2059	0.22639
498	0.12779	0.17012	0.18651	0.19421	0.20555	0.22469
502	0.13235	0.17137	0.18687	0.19409	0.20432	0.22289
506	0.13666	0.17328	0.18651	0.19295	0.20297	0.2197
510	0.14085	0.17436	0.18629	0.19223	0.20151	0.21687
514	0.14505	0.17679	0.18634	0.19122	0.20084	0.21413
518	0.14935	0.17879	0.18674	0.19124	0.20015	0.21252
522	0.15456	0.1819	0.18811	0.19168	0.20074	0.21085
526	0.15854	0.1833	0.18938	0.19279	0.20056	0.21121
530	0.16171	0.18484	0.18951	0.19225	0.20013	0.20932
534	0.16315	0.18338	0.18884	0.19183	0.19814	0.20821
538	0.16389	0.18285	0.1873	0.19009	0.1958	0.20526
542	0.16409	0.18159	0.18515	0.18739	0.19322	0.2016
546	0.16232	0.17924	0.18166	0.18369	0.18971	0.19667
550	0.15723	0.17281	0.1752	0.17686	0.18259	0.18944
554	0.15074	0.16566	0.16728	0.16895	0.17447	0.18037
558	0.14258	0.15672	0.15814	0.15952	0.16496	0.17059
562	0.13683	0.14882	0.15065	0.15221	0.15726	0.16263

Appendix A-1(cont.)
Uv-vis Spectrophotometric Data for C₆₀/Aniline (cont.)

Wavelength	0 M Aniline	0.5 M Aniline	0.85 M Aniline	1.0 M Aniline	1.15 M Aniline	1.5M Aniline
566	0.13443	0.14204	0.14771	0.15033	0.1519	0.16078
570	0.13309	0.13699	0.14755	0.1519	0.14758	0.16347
574	0.13094	0.1326	0.14565	0.15092	0.14395	0.16289
578	0.12682	0.12689	0.14041	0.14558	0.13899	0.15733
582	0.12492	0.12672	0.13574	0.14055	0.1362	0.15033
586	0.12849	0.13019	0.13838	0.14194	0.13785	0.15158
590	0.13681	0.14014	0.14441	0.14688	0.14468	0.15454
594	0.1436	0.14774	0.15024	0.15184	0.15135	0.15877
598	0.14342	0.14523	0.15094	0.15335	0.15067	0.16072
602	0.14149	0.14561	0.14813	0.14987	0.14952	0.15663
606	0.12865	0.1313	0.13689	0.13953	0.13736	0.14703
610	0.10779	0.11314	0.11559	0.1172	0.11812	0.12401
614	0.09207	0.09473	0.09879	0.10091	0.10083	0.10709
618	0.08269	0.08681	0.08737	0.08826	0.09024	0.09343
622	0.07741	0.07924	0.08095	0.08171	0.08304	0.08591
626	0.07341	0.07732	0.07539	0.07536	0.0788	0.07858
630	0.0611	0.06705	0.06328	0.06281	0.06775	0.06645
634	0.04677	0.05157	0.04939	0.04898	0.05309	0.05325
638	0.03577	0.03925	0.03789	0.03772	0.04112	0.04167
642	0.02888	0.03348	0.02957	0.02914	0.03369	0.03221
646	0.02255	0.02756	0.02367	0.02243	0.02725	0.0255
650	0.01843	0.02344	0.01929	0.01871	0.02304	0.02112
654	0.01649	0.02486	0.0182	0.01704	0.021	0.01974
658	0.01524	0.02402	0.0166	0.01476	0.01869	0.01576
662	0.0112	0.01628	0.01244	0.01248	0.01588	0.01422
666	0.00888	0.01489	0.00981	0.00859	0.01373	0.01024
670	0.00735	0.01067	0.00807	0.0076	0.01083	0.00897
674	0.0063	0.01045	0.00577	0.00432	0.00963	0.00403
678	0.00478	0.00731	0.00496	0.00497	0.00691	0.00549
682	0.00453	0.00931	0.00348	0.00201	0.00681	0.00224
686	0.00403	0.00928	0.00218	0.00066	0.00583	0.00029
690	0.00325	0.00745	0.00201	0.00067	0.0051	0.0004
694	0.00304	0.00894	0.00081	-0.00084	0.00468	-0.00157
698	0.00241	0.00822	0.00023	-0.0018	0.00412	-0.0026

Appendix B-1
Benesi-Hildebrand Data for C₆₀/Aniline

1/[Aniline]	1/Absorbance
2.00000	14.51800
1.66667	12.35178
1.17647	9.38527
1.11111	8.88099
1.05263	8.76732
1.00000	8.21693
0.94967	7.81128
0.86881	7.40302
0.65147	5.79542

Appendix B-2

Summary of Analysis of Data for Benesi-Hildebrand Data for C₆₀/Aniline

Regression Stat's	
Multiple R	0.9990
R Square	0.9981
Adjusted R Square	0.9978
Standard Error	2.50E-05
Observations	9

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	2.25E-06	2.25E-06	3.59E+03	9.48E-11
Residual	7	4.38E-09	6.26E-10		
Total	8	2.25E-06			

	Coef.	Std. Err.	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.000%	Upper 95.000%
Intercept	3.68E-04	3.68E-04	14.101	2.14E-06	3.06E-04	4.29E-04	3.06E-04	4.29E-04
X Variable 1	1.27E-03	2.12E-05	59.905	9.48E-11	1.22E-03	1.32E-03	1.22E-03	1.32E-03

minimum
0.2643

maximum
0.3150

Diff %
8.61724

K value
0.2892

Appendix C-1
Uv-vis Spectrophotometric Data for C₆₀/Substituted Anilines

Wavelength	aniline	o-toluidine	2,6-dimethylaniline	N-methylaniline	N,N-dimethylaniline
800	0.0046	0.0004	0.0002	-0.0007	-0.00715
796	0.0051	0.0013	-0.0002	2.68E-05	-0.00701
792	0.0041	2.97E-06	1.51E-06	-0.002	-0.00735
788	0.0051	0.0011	-0.0001	-0.0008	-0.00695
784	0.0039	-0.0003	-0.0003	-0.0011	-0.00730
780	0.0038	4.33E-05	-0.0008	-0.0007	-0.00705
776	0.0044	0.0012	-0.0006	-0.0004	-0.00715
772	0.0033	0.0009	-0.0013	-0.001	-0.00680
768	0.0036	0.0002	-0.0009	-0.0008	-0.00680
764	0.0045	0.0014	-0.0003	-0.0005	-0.00645
760	0.0037	-0.0002	-0.0003	-0.0012	-0.00640
756	0.0033	0.0006	-0.0001	-0.0005	-0.00600
752	0.0031	-0.0009	-0.0014	-0.0009	-0.00620
748	0.0035	-0.0004	-0.0014	-0.0008	-0.00605
744	0.0031	0.0003	-0.0016	-0.0003	-0.00550
740	0.0027	-0.0005	-0.0013	-0.0013	-0.00560
736	0.0038	0.0004	-0.001	-0.0004	-0.00485
732	0.004	0.0002	-0.0008	-0.0001	-0.00420
728	0.003	-0.0001	-0.0017	-0.0009	-0.00400
724	0.0025	3.73E-05	-0.0015	-0.0002	-0.00395
720	0.0032	-0.0001	-0.0007	-0.0002	-0.00320
716	0.0032	-0.0002	-0.0012	0.0001	-0.00265
712	0.0027	2.38E-05	-0.0011	0.0005	-0.00215
708	0.0029	-0.0012	-0.0013	0.0006	-0.00130
704	0.0029	-0.0001	-0.0012	4.38E-05	-0.00055
700	0.0026	0.0002	-0.0006	0.0008	0.00065
696	0.002	-0.0008	-0.001	0.0015	0.00170
692	0.0018	-0.0002	-0.0007	0.0012	0.00265
688	0.0025	0.0007	-0.0003	0.0027	0.00410
684	0.002	-2.0E-05	0.0001	0.002	0.00515
680	0.0022	0.0007	0.0003	0.0033	0.00670
676	0.0021	0.0003	0.001	0.0044	0.00820
672	0.0021	-1.3E-05	0.0017	0.0047	0.00935
668	0.0019	0.0009	0.0015	0.0049	0.01070
664	0.0026	0.0012	0.0034	0.0068	0.01245
660	0.0019	0.0017	0.0035	0.0072	0.01335
656	0.0034	0.0028	0.0052	0.0092	0.01475
652	0.0033	0.0032	0.0055	0.0095	0.01550
648	0.0032	0.0035	0.0053	0.0098	0.01575
644	0.0031	0.0032	0.0055	0.0103	0.01700
640	0.0035	0.0036	0.0064	0.0106	0.01795

Appendix C-1 (cont.)
Uv-vis Spectrophotometric Data for C₆₀/Substituted Anilines

Wavelength	aniline	o-toluidine	2,6-dimethylaniline	N-methylaniline	N,N-dimethylaniline
636	0.0034	0.0044	0.0069	0.0116	0.01970
632	0.0037	0.0044	0.0075	0.0124	0.02165
628	0.0043	0.0059	0.0089	0.014	0.0243
624	0.0048	0.0063	0.0103	0.0156	0.0265
620	0.005	0.0056	0.0105	0.0165	0.0284
616	0.0036	0.0062	0.0099	0.0164	0.0290
612	0.0041	0.0061	0.0105	0.0177	0.0312
608	0.0046	0.0081	0.0135	0.02	0.0344
604	0.0055	0.0098	0.0163	0.0229	0.0369
600	0.0072	0.0106	0.0188	0.0253	0.0393
596	0.0068	0.0106	0.0174	0.0249	0.0391
592	0.0053	0.0095	0.0155	0.0243	0.0384
588	0.0057	0.0089	0.0162	0.0253	0.0395
584	0.0042	0.0094	0.0162	0.026	0.0405
580	0.004	0.009	0.0176	0.0268	0.0421
576	0.0058	0.0106	0.021	0.0293	0.0453
572	0.0064	0.0131	0.0228	0.033	0.0477
568	0.0066	0.0135	0.0242	0.0342	0.0497
564	0.0067	0.0139	0.026	0.0358	0.0507
560	0.0073	0.0156	0.027	0.0374	0.0520
556	0.0082	0.0162	0.0301	0.0399	0.0543
552	0.01	0.0189	0.0323	0.0428	0.0563
548	0.0107	0.0202	0.0349	0.046	0.0588
544	0.0107	0.0199	0.036	0.0469	0.0592
540	0.0113	0.0222	0.0382	0.0489	0.0600
536	0.0119	0.0235	0.0399	0.0513	0.0608
532	0.0126	0.0247	0.0418	0.0529	0.0614
528	0.014	0.0266	0.0447	0.0558	0.0627
524	0.0146	0.0283	0.0469	0.0574	0.0627
520	0.0158	0.0307	0.0509	0.0594	0.0634
516	0.0172	0.0333	0.0529	0.0619	0.0635
512	0.0188	0.0346	0.0567	0.0634	0.0639
508	0.0206	0.0388	0.0608	0.0655	0.0646
504	0.0223	0.0413	0.064	0.0675	0.0643
500	0.0255	0.0451	0.0687	0.0679	0.0646
496	0.0276	0.0491	0.0718	0.0702	0.0644
492	0.0302	0.0515	0.0756	0.0707	0.0644
488	0.0331	0.0558	0.0782	0.0715	0.0635
484	0.0369	0.0597	0.0822	0.0719	0.0632
480	0.0401	0.0628	0.0854	0.0721	0.0623
476	0.0436	0.0673	0.0881	0.0723	0.0612

Appendix C-1 (cont.)
Uv-vis Spectrophotometric Data C₆₀/Substituted Anilines

Wavelength	aniline	o-toluidine	2,6-dimethylaniline	N-methylaniline	N,N-dimethylaniline
472	0.0463	0.0695	0.0896	0.0706	0.0599
468	0.0505	0.0731	0.0919	0.0688	0.0583
464	0.0543	0.0766	0.0931	0.069	0.0570
460	0.0587	0.0787	0.094	0.0669	0.0557
456	0.0619	0.0819	0.0948	0.0661	0.0541
452	0.0644	0.0831	0.094	0.064	0.0523
448	0.0677	0.0843	0.0944	0.0627	0.0509
444	0.0701	0.0865	0.0925	0.0601	0.04865
440	0.0727	0.086	0.0906	0.0578	0.04685
436	0.0744	0.0863	0.0888	0.055	0.0448
432	0.0766	0.0865	0.0872	0.0544	0.04365
428	0.0773	0.0845	0.0845	0.051	0.0419
424	0.0787	0.0851	0.0837	0.0499	0.0416
420	0.0789	0.0831	0.082	0.0486	0.0416
416	0.078	0.081	0.0825	0.0471	0.0431

Appendix C-2 (cont.)
Uv-vis Spectrophotometric Data for C₆₀/Substituted Anilines

Wavelength	N,N-diethylaniline	Wavelength	N,N-diethylaniline	Wavelength	N,N-diethylaniline
800	0.02480	636	0.04820	472	0.0303
796	0.02533	632	0.04947	468	0.0265
792	0.02507	628	0.0513	464	0.0245
788	0.02513	624	0.0533	460	0.0213
784	0.02493	620	0.0535	456	0.0190
780	0.02493	616	0.0540	452	0.0162
776	0.02547	612	0.0554	448	0.0141
772	0.02527	608	0.0569	444	0.012267
768	0.02580	604	0.0585	440	0.010333
764	0.02633	600	0.0590	436	0.0094
760	0.02587	596	0.0583	432	0.0094
756	0.02633	592	0.0577	428	0.009333
752	0.02640	588	0.0579	424	0.011133
748	0.02660	584	0.0581	420	0.0134
744	0.02767	580	0.0586	416	0.0158
740	0.02707	576	0.0599		
736	0.02853	572	0.0616		
732	0.02940	568	0.0613		
728	0.02907	564	0.0611		
724	0.02953	560	0.0617		
720	0.03040	556	0.0619		
716	0.03120	552	0.0626		
712	0.03187	548	0.0631		
708	0.03240	544	0.0615		
704	0.03313	540	0.0613		
700	0.03473	536	0.0607		
696	0.03493	532	0.0594		
692	0.03573	528	0.0593		
688	0.03767	524	0.0576		
684	0.03807	520	0.0566		
680	0.03973	516	0.0556		
676	0.04047	512	0.0535		
672	0.04100	508	0.0524		
668	0.04260	504	0.0501		
664	0.04327	500	0.0484		
660	0.04360	496	0.0463		
656	0.04460	492	0.0437		
652	0.04473	488	0.0416		
648	0.04507	484	0.0391		
644	0.04580	480	0.0358		
640	0.04660	476	0.0335		

Appendix D-1

Spectrophotometric Data for Benesi-Hildebrand Determination of K for C₆₀/Naphthalene

Corrected Data at 15°C		Corrected Data at 25°C		Corrected Data at 32°C	
1/[Naphthalene]	1/ΔAbs	1/[Naphthalene]	1/ΔAbs	1/[Naphthalene]	1/ΔAbs
0.8355	2.9453	1.6469	5.6136	1.6596	5.7127
0.8359	2.8521	1.3175	4.4984	1.3277	4.5660
0.8563	2.8369	1.0979	3.8398	1.1064	3.9208
0.9053	2.9861	0.9411	3.3172	0.9483	3.3697
0.9054	3.0808	0.8446	3.0252	0.8511	3.0798
0.9134	3.0199	1.8302	6.0500	1.8443	6.1835
0.9310	3.2134	1.4642	4.7856	1.4754	4.8919
0.9518	3.3385	1.1979	4.0437	1.2072	4.1327
0.9786	3.3166	1.0981	3.5966	1.1066	3.6922
1.0028	3.3295	1.0136	3.4446	1.0215	3.5599
1.0349	3.3735	1.7341	5.7961	1.7475	5.9734
1.0502	3.4919	1.3448	4.3948	1.3552	4.5376
1.0539	3.4191	1.1561	3.8314	1.1650	3.9590
1.0862	3.7157	0.9152	3.1461	0.9223	3.2519
1.0864	3.5461	2.1966	7.2291	2.2135	7.6336
1.1437	3.7255	1.5691	5.1696	1.5812	5.3402
1.1714	4.0252	1.3449	4.5721	1.3553	4.6561
1.1851	3.9268	1.2434	4.1302	1.2530	4.1818
1.2301	4.0227	1.0461	3.4855	1.0541	3.5534
1.2690	4.0744	0.8449	2.9398	0.8514	2.9915
1.3034	4.3405	2.3682	7.7233	2.8203	9.3350
1.3304	4.1480	2.0524	6.6055	2.3864	8.0140
1.3305	4.4737	1.6203	5.3731	2.0682	6.8274
1.4485	4.6479	1.5397	5.1552	1.6328	5.5518
1.5228	4.9548	1.2828	4.2234	1.5516	5.2851
1.5523	5.0221	0.9621	3.3388	1.2926	4.3064
1.6030	5.2725	1.8109	5.8978	1.1932	4.2826
1.6293	5.4771	0.9151	3.0897	1.0698	3.7236
1.7156	5.5941	1.0653	3.5212	0.9695	3.3791
1.7916	5.8013	0.9892	3.4650	1.8249	6.0449
1.8106	5.8551	0.9233	3.1363	0.9222	3.1652
2.0304	6.4283	0.8656	2.9635	1.0735	3.5903
2.1731	6.9037	0.8146	2.7857	0.9968	3.5346
2.3428	7.4599	0.7694	2.6500	0.9304	3.1942
		1.5388	5.0968		
		1.4578	4.9094		
		1.2043	4.0129		
		0.9892	3.3416		
		0.8702	3.6356		

Appendix D-1 (cont.)
Spectrophotometric Data for Benesi-Hildebrand
Determination of K For C₆₀/Naphthalene

Corrected Data at 40°C	
1/[Naphthalene]	1/ΔAbs
1.6744	5.9701
1.1163	4.0566
0.9568	3.4858
0.8587	3.1858
1.8608	6.3561
1.4886	5.0373
1.2180	4.2301
1.1165	3.7777
1.0306	3.6340
1.7631	6.1637
1.3673	4.6731
1.1754	4.0486
0.9305	3.3095
2.2333	7.7888
1.5953	5.4348
1.3674	4.8045
1.2642	4.3156
1.0635	3.6352
0.8590	3.0520
2.8455	9.6258
2.4077	8.3071
2.0867	7.0206
1.6474	5.7098
1.5655	5.4303
1.3042	4.4364
1.2039	4.4455
1.0793	3.8220
0.9781	3.4704
1.8412	6.2700
0.9304	3.2588
1.0831	3.6885
1.0057	3.6534
0.9387	3.2757

Appendix D-2
Summary Analysis of Benesi-Hildebrand Data at 15°C and K Calculation
for C60/Naphthalene

Regression Stat.'s	
Multiple R	0.9975
R Square	0.9951
Adjusted R Square	0.9949
Standard Error	0.0876
Observations	34

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	49.59	49.587	6.46E+03	1.69E-38
Residual	32	0.2455	7.67E-03		
Total	33	49.83			

	Coef.	Std. Err.	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.2856	0.0516	5.535	4.18E-06	0.1805	0.3906	0.1805	0.3906
X Variable 1	3.0654	0.0381	80.400	1.69E-38	2.9877	3.1430	2.9877	3.1430

K 0.0932 0.0182 %
 0.1955

Kmin 0.0754
 Kmax 0.1114

ke max 0.3222
 ke min 0.3303

Appendix D-3
Summary of Analysis of Benesi-Hildebrand Data at 25°C and K Calculation
for C₆₀/Naphthalene

Regression Stat.'s	
Multiple R	0.9984
R Square	0.9969
Adjusted R Square	0.9968
Standard Error	0.0717
Observations	39

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	60.4906	60.4906	1.18E+04	6.261E-48
Residual	37	0.1903	5.14E-03		
Total	38	60.6808			

	Coef.	Std. Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.2520	0.0391	6.4481	1.56E-07	0.1728	0.3312	0.1728	0.3312
X Variable 1	3.1552	0.0291	108.463	6.26E-48	3.0963	3.2142	3.0963	3.2142

K 0.0799 0.0132 %
 0.1658

Kmin 0.0669
 Kmax 0.0931

ke max 0.3140
 ke min 0.3199

Appendix D-4
Summary of Analysis of Benesi-Hildebrand Data at 32°C and K Calculation
C₆₀/Naphthalene

Regression Stat.'s	
Multiple R	0.9984
R Square	0.9968
Adjusted R Square	0.9967
Standard Error	0.0895
Observations	34

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	78.58	78.58	9.82E+03	2.15E-41
Residual	32	0.2560	8.00E-03		
Total	33	78.8384			

	Coef.	Std. Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.2115	0.0477	4.4325	1.02E-04	0.1143	0.3087	0.1143	0.3087
X Variable 1	3.2543	0.0328	99.1012	2.15E-41	3.1874	3.3212	3.1874	3.3212

K 0.0650 0.0155 %
 0.2381

Kmin 0.0498

Kmax 0.0805

ke max 0.3042

ke min 0.3104

Appendix D-5
Summary of Analysis of Benesi-Hildebrand Data at 40°C and K Calculation
for C₆₀/Naphthalene

Regression Stat.'s	
Multiple R	0.9981
R Square	0.9962
Adjusted R Square	0.9961
Standard Error	0.1015
Observations	33

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	83.8944	#####	8146.5020	4.2074E-39
Residual	31	0.3192	0.0103		
Total	32	84.2136			

	Coef.	Std. Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.1976	0.0543	3.6409	9.8006E-04	0.0869	0.3083	0.0869	0.3083
X Variable 1	3.3332	0.0369	#####	4.2074E-39	3.2579	3.4086	3.2579	3.4086

K 0.0593 0.0171 %
 0.2889

Kmin 0.0425
 Kmax 0.0764

ke max 0.2967
 ke min 0.3034

Appendix E-1
Data for Enthalpy Calculation For C₆₀/Naphthalene

Temperature	T (K)	1/T	ke	ln ke	ke max	ke min	ln kemax diff	ln kemin diff	regr
15	288.2	0.0035	806.2400	6.6924	816.3995	796.3406	0.0125	0.0124	6.6942
25	298.2	0.0034	791.7500	6.6742	799.1248	784.5240	0.0093	0.0092	6.6698
32	305.2	0.0033	773.5600	6.6510	781.4483	765.8352	0.0101	0.0100	6.6536
40	313.2	0.0032	761.9950	6.6359	770.5317	753.6448	0.0111	0.0110	6.6360

Appendix E-2
Summary of Analysis of Data for Enthalpy and Entropy Calculation
for C60/Naphthalene

Regression Stat.'s	
Multiple R	0.9919
R Square	0.9838
Adjusted R Square	0.9757
Standard Error	3.89E-03
Observations	4

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	1.84E-03	1.84E-03	121.5067	8.1298E-03
Residual	2	3.02E-05	1.51E-05		
Total	3	1.87E-03			

	Coef.	Std. Err.	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	5.9654	0.0634	94.160	1.128E-04	5.6928	6.2380	5.6928	6.2380
1/T	210.012	19.052	11.023	8.130E-03	128.037	291.99	128.037	291.987

ENTROPY (J/mole-K)

49.5961

ENTHALPY (kJ/mole)

1.7460

Appendix F-1

Data for Benesi-Hildebrand Determination of K for C60/Phenanthrene
at 20°C

[Phen.]	C60 ABS @423 nm	ABS @ 423 nm	Δ ABS @ 423nm	[C60]	1/[Phen]	[C60]/ Δ ABS @ 423 nm
1.0837	0.2117	1.1623	0.9506	5.17E-04	0.9227	5.4419E-04
0.9752	0.2117	1.0758	0.8641	5.17E-04	1.0255	5.9866E-04
0.8666	0.2117	0.9954	0.7837	5.17E-04	1.1540	6.6008E-04
0.7560	0.2117	0.8731	0.6614	5.17E-04	1.3228	7.8213E-04
0.6504	0.2117	0.8238	0.6121	5.17E-04	1.5374	8.4513E-04
0.5409	0.2117	0.7680	0.5563	5.17E-04	1.8489	9.2990E-04
0.4333	0.2117	0.6537	0.4420	5.17E-04	2.3079	1.1704E-03
0.3519	0.2117	0.5839	0.3722	5.17E-04	2.8420	1.3899E-03

Appendix F-2
Summary of Analysis of Benesi-Hildebrand Data at 20°C and K
Calculation For C₆₀/Phenanthrene

Regression Stat.'s	
Multiple R	0.9966
R Square	0.9932
Adjusted R Square	0.9921
Standard Error	2.596E-05
Observations	8

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	5.92E-07	5.921E-07	878.5977	9.776E-08
Residual	6	4.04E-09	6.740E-10		
Total	7	5.96E-07			

	Coef.	Std. Err	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.650E-04	2.53E-05	6.51E+00	6.25E-04	1.03E-04	2.270E-04	1.030E-04	2.270E-04
1/[Phenan]	4.322E-04	1.46E-05	2.96E+01	9.78E-08	3.96E-04	4.679E-04	3.965E-04	4.679E-04

minimum
0.3127

maximum
0.4559

Diff %
18.1181

K value
0.3818

Appendix G-1

Data for Benesi-Hildebrand Determination of K for C60/Phenanthrene at 25°C

[Phen]	C60 ABS @423 nm	ABS @ 423 nm	Δ ABS @ 423nm	[c60]	1/[Phen]	[C60]/ Δ ABS @ 423 nm
1.078	2.133E-01	1.1508	0.9375	5.15E-04	0.9276	5.4887E-04
0.97	2.133E-01	1.0651	0.8518	5.15E-04	1.0309	6.0410E-04
0.862	2.133E-01	0.9869	0.7736	5.15E-04	1.1601	6.6516E-04
0.752	2.133E-01	0.8657	0.6524	5.15E-04	1.3298	7.8873E-04
0.647	2.133E-01	0.8168	0.6035	5.15E-04	1.5456	8.5264E-04
0.538	2.133E-01	0.7626	0.5493	5.15E-04	1.8587	9.3677E-04
0.431	2.133E-01	0.6469	0.4336	5.15E-04	2.3202	1.1867E-03
0.35	2.133E-01	0.5778	0.3645	5.15E-04	2.8571	1.4117E-03

Appendix G-2
Summary of Analysis of Benesi-Hildebrand Data at 25°C and K
Calculation For C₆₀/Phenanthrene

Regression Stat's	
Multiple R	0.9966
R Square	0.9931
Adjusted R Square	0.9920
Standard Error	2.663E-05
Observations	8

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	6.165E-07	6.165E-07	869.6780	1.008E-07
Residual	6	4.253E-09	7.089E-10		
Total	7	6.208E-07			

	Coef.	Std. Err.	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.600E-04	2.599E-05	6.1548	8.435E-04	9.636E-05	2.236E-04	9.636E-05	2.236E-04
1/[Phenan]	4.386E-04	1.487E-05	29.4903	1.008E-07	4.022E-04	4.750E-04	4.022E-04	4.750E-04

minimum
0.2954

maximum
0.4388

Diff %
18.9943

K value
0.3647

Appendix H-1

Data for Benesi-Hildebrand Determination of K for C60/Phenanthrene at 30°C

[Phen]	C60 ABS @423 nm	ABS @ 423 nm	Δ ABS @ 423nm	[C60]	1/[Phen]	[C60]/ Δ ABS @ 423 nm
1.0721	0.2152	1.1402	0.9250	5.12E-04	0.9327	5.5326E-04
0.9647	0.2152	1.0551	0.8399	5.12E-04	1.0366	6.0931E-04
0.8573	0.2152	0.9769	0.7617	5.12E-04	1.1665	6.7187E-04
0.7479	0.2152	0.8567	0.6415	5.12E-04	1.3371	7.9776E-04
0.6435	0.2152	0.8096	0.5944	5.12E-04	1.5541	8.6097E-04
0.5351	0.2152	0.7242	0.5090	5.12E-04	1.8689	1.0054E-03
0.4287	0.2152	0.6361	0.4209	5.12E-04	2.3329	1.2159E-03
0.3481	0.2152	0.5733	0.3581	5.12E-04	2.8728	1.4291E-03

Appendix H-2
Summary of Analysis of Benesi-Hildebrand Data at 30°C and K
Calculation For C₆₀/Phenanthrene

Regression Stat.'s	
Multiple R	0.9978
R Square	0.9955
Adjusted R Square	0.9948
Standard Error	2.22E-05
Observations	8

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	6.56E-07	6.56E-07	1.33E+03	2.82E-08
Residual	6	2.96E-09	4.93E-10		
Total	7	6.59E-07			

	Coef.	Std. Err.	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.56E-04	2.17E-05	7.196	3.64E-04	1.03E-04	2.09E-04	1.03E-04	2.09E-04
1/[Phenan]	4.50E-04	1.23E-05	36.498	2.82E-08	4.20E-04	4.80E-04	4.20E-04	4.80E-04

minimum
0.2903

maximum
0.4057

Diff %
16.1920

K value
0.3464

Appendix I-1
Data for Benesi-Hildebrand Determination of K for C₆₀/Phenanthrene
at 35°C

Conc.	C60 ABS @423 nm	ABS @ 423 nm	Δ ABS @ 423nm	[c60]	1/[Phenan]	[C60]/Δ ABS @ 423 nm
1.0662	0.2166	1.1291	0.9125	5.09E-04	0.9379	5.5775E-04
0.9594	0.2166	1.0453	0.8287	5.09E-04	1.0423	6.1415E-04
0.8526	0.2166	0.9668	0.7502	5.09E-04	1.1729	6.7841E-04
0.7438	0.2166	0.8499	0.6333	5.09E-04	1.3445	8.0364E-04
0.6399	0.2166	0.8006	0.5840	5.09E-04	1.5627	8.7148E-04
0.5321	0.2166	0.7202	0.5036	5.09E-04	1.8793	1.0106E-03
0.4263	0.2166	0.6427	0.4261	5.09E-04	2.3458	1.1944E-03
0.3462	0.2252	0.5566	0.3314	4.88E-04	2.8887	1.4717E-03

Appendix I-2
Summary of Analysis of Benesi-Hildebrand Data at 35°C and K
Calculation For C₆₀/Phenanthrene

Regression Stat.'s	
Multiple R	0.9978
R Square	0.9957
Adjusted R Square	0.9950
Standard Error	2.22E-05
Observations	8

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	6.81E-07	6.81E-07	1.38E+03	2.53E-08
Residual	6	2.96E-09	4.93E-10		
Total	7	6.84E-07			

	Coef.	Std. Err.	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.50E-04	2.17E-05	6.90E+00	4.57E-04	9.65E-05	2.03E-04	9.65E-05	2.03E-04
1/[Phenan]	4.56E-04	1.23E-05	3.72E+01	2.53E-08	4.26E-04	4.86E-04	4.26E-04	4.86E-04

minimum
0.2731

maximum
0.3859

Diff %
16.7273

K value
0.3280

Appendix J-1
Data for Enthalpy Calculation For C₆₀/Phenanthrene

TEMP(°C)	TEMP (K)	1/TEMP	K corr	ln 1/K corr	% Diff	Error	K _E corr	ln (1/K _E corr)
20	293.15	3.411E-03	0.3818	0.9627	18.118	0.0692	2313.88	7.7467
25	298.15	3.354E-03	0.3647	1.0087	18.994	0.0693	2279.96	7.7319
30	303.15	3.299E-03	0.3464	1.0601	16.192	0.0561	2221.99	7.7062
35	308.15	3.245E-03	0.3280	1.1147	16.727	0.0549	2193.53	7.6933

Appendix J-2
Summary of Analysis of van't Hoff Analysis and Enthalpy Calculation
For C₆₀/Phenanthrene

Regression Stat.'s	
Multiple R	0.9918
R Square	0.9837
Adjusted R Square	0.9756
Standard Error	3.78E-03
Observations	4

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	1.73E-03	1.73E-03	1.21E+02	8.16E-03
Residual	2	2.86E-05	1.43E-05		
Total	3	1.76E-03			

	Coef.	Std. Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	6.6012	0.1017	64.9247	2.37E-04	6.1638	7.0387	6.1638	7.0387
1/TEMP	336.095	30.5528	11.0005	8.16E-03	204.64	467.5531	204.6	467.55

ENTROPY

-54.8826

ENTHALPY

2.7943

Appendix K-1
Data for Benesi-Hildebrand Determination of K for C₆₀/Pyrene at 25°C

conc	abs @ 506 nm	abs @ 800 nm	506 nm cor	dif	1/dif	1/con	line
0	0.27054	0.00757	0.26297	—	—	—	—
0.1454	0.3628	0.0111	0.3518	0.0888	11.2600	6.8766	11.2064
0.1745	0.3718	0.0047	0.3671	0.1041	9.6061	5.7305	9.6083
0.2036	0.3740	-0.0067	0.3807	0.1177	8.4940	4.9119	8.4668
0.2269	0.3818	-0.0095	0.3913	0.1283	7.7942	4.4081	7.7643
0.1323	0.3388	0.0009	0.3379	0.0818	12.2234	7.5586	12.1573
0.1617	0.3318	-0.0212	0.3530	0.0969	10.3242	6.1843	10.2410
0.1955	0.3877	0.0145	0.3731	0.1171	8.5434	5.1148	8.7498
0.2205	0.3583	-0.0238	0.3822	0.1261	7.9321	4.5351	7.9415
0.1413	0.3400	-0.0037	0.3437	0.0888	11.2651	7.0756	11.4838
0.1649	0.3484	-0.0050	0.3533	0.0984	10.1626	6.0648	10.0744
0.1826	0.3897	0.0274	0.3622	0.1073	9.3197	5.4779	9.2560
0.1958	0.3701	0.0011	0.3690	0.1141	8.7642	5.1072	8.7391

Appendix K-2

Summary of Analysis of Benesi-Hildebrand Data at 25°C and K Calculation For C₆₀/Pyrene

Regression Stat. 's	
Multiple R	0.9914
R Square	0.9829
Adjusted R Square	0.9822
Standard Error	0.1879
Observations	27

ANOVA					
	df	SS	MS	F	Sign. F
Regression	1	50.7699	50.7699	1438.70	1.28E-23
Residual	25	0.8822	0.0353		
Total	26	51.6521			

	Coeff.	Standard Err	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.4819	0.2119	6.9919	2.50E-07	1.0454	1.9184	1.0454	1.9184
X Variable 1	1.4049	0.0370	37.9302	1.28E-23	1.3287	1.4812	1.3287	1.4812

minimum
0.8807

maximum
1.2383

Diff %
16.5037

K_ε
0.7118

K value
1.0548

Appendix L-1
Volume Corrections
for Expansion of Toluene

temp °C	v_t	$v_t/v_{25^\circ\text{C}}$
15	1.016	0.989
20	1.021	0.995
25	1.027	1.000
30	1.032	1.005
32	1.035	1.008
35	1.038	1.011
40	1.044	1.017