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Ground state charge transfer complex of [84]fullerene and *N*,*N*-diethylaniline

Christopher E. Bunker, Harry W. Rollins and Ya-Ping Sun *

Department of Chemistry, Howard L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-1905, USA

The formation of the [84]fullerene–*N*,*N*-diethylaniline ground state charge transfer complex at different *N*,*N*-diethylaniline concentrations and temperatures has been studied by absorption spectroscopy and by use of a chemometric method principal component analysis to determine the absorption spectrum of the complex and the thermodynamic parameters of the C_{84} monomer–complex equilibrium.

[84]Fullerene (C_{84}) is one of the larger carbon cages produced in relatively abundant quantities in fullerene soot.[1,2] For [60]fullerene (C_{60}) and [70]fullerene (C_{70}), it has been established that the fullerene molecules are excellent electron acceptors, forming ground and excited state charge transfer complexes with electron donors such as aromatic amines.[3–6] Here we report the observation of C_{84} ground state charge transfer complex with *N*,*N*-diethylaniline (DEA), and the spectroscopic characterization of the complex formation equilibrium.

C_{84} was obtained from fullerene soot (MER Co.) *via* a two-step HPLC separation and purification procedure. The purity of the C_{84} sample was examined by matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF, Kratos Kompact III), and only a single C_{84} peak was observed (Fig. 1).

N,*N*-Diethylaniline (Aldrich, 99+%) was purified by distillation under reduced pressure. Spectrophotometry grade toluene (Burdick & Jackson) was used as received. All absorption measurements were performed on a Shimadzu UV-3100 UV–VIS–NIR spectrophotometer. Temperature variations in the measurements were accomplished through fluid circulation. A Haake K20 circulating bath and a DC3 controller were used to keep the sample solution at a constant temperature. The actual temperature of the sample solution was monitored by use of an Omega DP116-KCl digital thermometer and a temperature probe in contact with the solution in the cuvette through a small hole in the cap. The accuracy in temperature reading is ±0.1 °C.

The absorption spectrum of C_{84} in toluene differs significantly from those of C_{60} and C_{70}, extending well into the near-infrared region (Fig. 1).[7,8] The molar absorptivities of C_{84} are larger than those of C_{60}, but smaller than those of C_{70}. The absorption spectrum of C_{84} in CS_2 is nearly unchanged from that in toluene. However, the spectrum in neat DEA is very different (Fig. 2). It is broader and not as well resolved as the spectrum in toluene. The observed molar absorptivities are also significantly higher in DEA than in toluene. Similar absorption spectral changes have been reported for C_{60} and C_{70} in DEA, which were attributed to the formation of fullerene–DEA ground state charge transfer complexes.[3–6] The changes in the absorption spectrum of C_{84} from toluene to DEA can also be attributed to the C_{84}–DEA complex formation. Absorption contribution of the complex is DEA concentration dependent. As shown in Fig. 2 for C_{84} in toluene–DEA mixtures, observed absorption spectra vary systematically with the concentration of DEA.

For C_{60} and C_{70}, the formation of 1:1 ground state complexes with DEA has been established.[6] A C_{84}–DEA 1:1 complex may also be expected. However, a complication for C_{84} is the possible presence of isomers. Theoretical calculations have identified 24 structures of C_{84} that all satisfy the isolated pentagon rule.[9,10] Experimentally, the precise number of stable C_{84} isomers in a room-temperature solution is still subject to debate.[2,11–18] Based on results from elegant ^{13}C NMR studies,[2,11–13] it has been suggested that there are only two major isomers (D_2 and D_{2d} symmetry) of C_{84} in solution with a 2:1 ratio of relative abundance. Quantitative experimental evidence for the presence of only a single $(\eta^2\text{-}C_{84})Ir(CO)Cl[P(C_6H_5)_3]_2$ crystalline adduct has also been reported.[18] With the possibility of multiple absorbing species, the observed absorption spectra of C_{84} in neat DEA and toluene–DEA mixtures were analysed by use of a chemometric method principal component analysis to determine the number of independent absorptions.

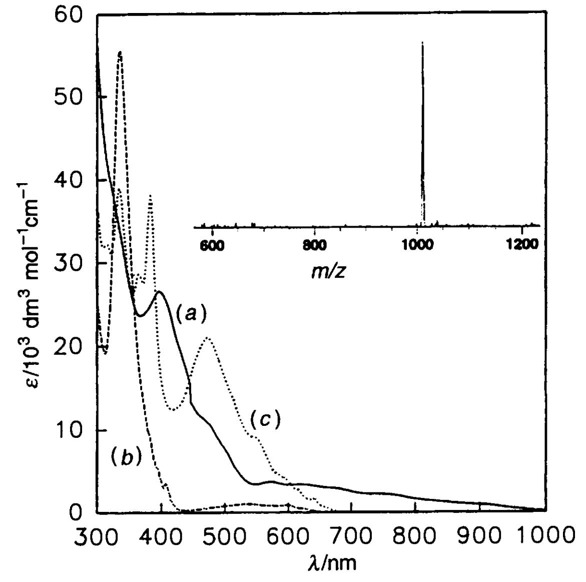

Fig. 1 The absorption spectra of (*a*) C_{84}; (*b*) C_{60}; and (*c*) C_{70}. The insert is the MALDI-TOF result of the C_{84} sample.

The theory and applications of principal component analysis have been described in detail in the literature.[19–21] Briefly, the analysis determines the number of significant components *k* in an *n*-dimensional data matrix ($k \leqslant n$). For the data matrix **Y** consisting of *n* experimental spectra as row vectors, the analysis enables a representation of the spectra in a *k*-dimensional vector space. The vector space is constructed by *k* significant eigenvectors of the matrix **Y**, which correspond to *k* significant eigenvalues. An experimental spectrum Y_i in the matrix **Y** can be represented as a linear combination of the significant eigenvectors V_j [eqn. (1)] where R_i is a residual vector

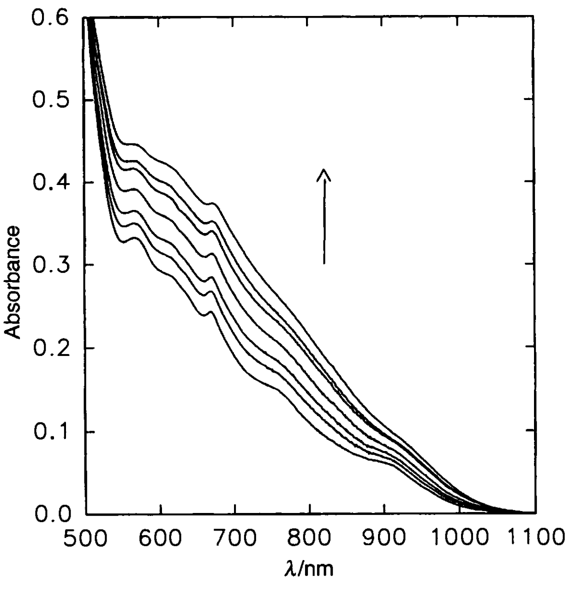

Fig. 2 Selected absorption spectra of C_{84} (1.9×10^{-5} mol dm^{-3} and 5 cm optical path length) in toluene at DEA concentrations of (in the direction of the arrow) 0, 0.83, 1.44, 2.38, 3.36, 4.79 and 6.23 (neat DEA) mol dm^{-3}

$$Y_i = \sum_{j=1}^{k} \xi_{ij} V_j + R_i \qquad (1)$$

consisting primarily of experimental noise. For the C_{84}–DEA complex formation, the data matrix consists of observed absorption spectra of C_{84} in toluene–DEA mixtures at different DEA volume fractions. The spectra were normalized such that the area under each spectrum is unity. Principal component analysis of the data matrix yields four largest eigenvalues of 0.3674, 9.269×10^{-2}, 1.322×10^{-3} and 1.000×10^{-3}, which correspond best to a two-component system. A plot of the combination coefficients ξ_{i2} *vs.* ξ_{i1} is linear, also consistent with a two-component system.[19–21]

The results of principal component analysis can be explained by absorptions of only a single C_{84} monomer and a C_{84}–DEA complex. It is also possible that the absorption spectra of the two most abundant C_{84} isomers are very similar,[22] as are the spectra of the corresponding complexes. If it is further assumed that the complexes of the two isomeric C_{84} species have the same formation constant K, eqn. (2) can be applied in either

$$(A_{\mathrm{OBS},\lambda} - A_{\mathrm{M},\lambda})/b = cK(\varepsilon_{\mathrm{C},\lambda} - \varepsilon_{\mathrm{M},\lambda})[\mathrm{DEA}]/(1 + K[\mathrm{DEA}]) \qquad (2)$$

case,[23] where b is the optical path length, ε represents molar absorptivities, c is the initial C_{84} concentration (the sum of concentrations in the case of two isomers), and the subscripts M and C denote monomer and complex, respectively. Eqn. (2) can be rearranged to the linear Benesi–Hildebrand plot [eqn. (3)],[24]

$$b\Delta A_\lambda^{-1} = (cK\Delta\varepsilon_\lambda)^{-1}[\mathrm{DEA}]^{-1} + (c\Delta\varepsilon_\lambda)^{-1} \qquad (3)$$

where $\Delta A_\lambda = A_{\mathrm{OBS},\lambda} - A_{\mathrm{M},\lambda}$, $\Delta\varepsilon_\lambda = \varepsilon_{\mathrm{C},\lambda} - \varepsilon_{\mathrm{M},\lambda}$. The equilibrium constant K can be obtained from the ratio intercept/slope. However, a determination of K at a single wavelength is typically sensitive to effects of uncertainties in the spectra at low complexing agent concentrations. The C_{84}–DEA system is no exception, especially because the variations in the absorption spectra over the entire DEA concentration range are relatively small. Thus, a global treatment was performed by normalizing eqn. (3) to give eqn. (4), where $\Delta A_{\mathrm{DEA},\lambda} = A_{\mathrm{DEA},\lambda} - A_{\mathrm{M},\lambda}$, with

$$b(\Delta A_\lambda/\Delta A_{\mathrm{DEA},\lambda})^{-1} = (cK\Delta\varepsilon_\lambda/\Delta A_{\mathrm{DEA},\lambda})^{-1}[\mathrm{DEA}]^{-1} + (c\Delta\varepsilon_\lambda/\Delta A_{\mathrm{DEA},\lambda})^{-1} \qquad (4)$$

$A_{\mathrm{DEA},\lambda}$ being the absorbance in neat DEA. A plot comprising four wavelengths (568, 621, 670 and 765 nm) is shown in Fig. 3, which yields a K value of 0.067 dm^3 mol^{-1}. A similar K value (0.069 dm^3 mol^{-1}) was obtained from a nonlinear least-squares regression based on eqn. (5). The formation constant of the C_{84}–DEA complex is very similar to those of the C_{60} and C_{70} complexes (0.07 ± 0.01 and 0.09 ± 0.01 dm^3 mol^{-1}, respectively).

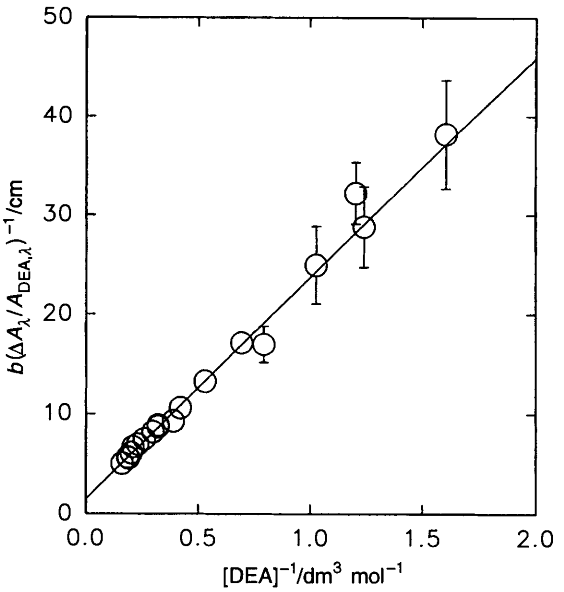

Fig. 3 A global Benesi–Hildebrand plot [eqn. (4)] for the C_{84}–DEA complex formation based on absorbance data at 568, 621, 670 and 765 nm. The line is from a linear least-squares regression (slope = 22.22 and intercept = 1.48).

The molar absorptivity of the complex at a given wavelength $\varepsilon_{\mathrm{C},\lambda}$ can also be obtained from eqn. (5). At 568 nm the molar

$$\varepsilon_{\mathrm{C},\lambda} = (\Delta A_\lambda/b)(1 + K[\mathrm{DEA}])/cK[\mathrm{DEA}] + \varepsilon_{\mathrm{M},\lambda} \qquad (5)$$

absorptivity of the C_{84}–DEA complex is 7400 dm^3 mol^{-1} cm^{-1}, which is much larger than that of the C_{84} monomer (3670 dm^3 mol^{-1} cm^{-1}). In principle, eqn. (5) can be applied at all wavelengths to obtain the pure absorption spectrum of the complex (Fig. 4). However, the calculation of $\varepsilon_{\mathrm{C},\lambda}$ in terms of eqn. (5) may be somewhat sensitive to experimental spectral noise at wavelengths where the absorption is relatively weak. Thus, the pure complex absorption spectrum was also obtained by using the eigenvectors from principal component analysis. As a two component system (C_{84} monomer and complex), the complex absorption spectrum S_{C} can be represented by the two largest eigenvectors V_1 and V_2 [eqn. (6)],[19–21] where $\xi_{\mathrm{C}1}$ and

$$S_{\mathrm{C}} = \xi_{\mathrm{C}1}V_1 + \xi_{\mathrm{C}2}V_2 \qquad (6)$$

$\xi_{\mathrm{C}2}$ are combination coefficients. Because the absorption spectra in the data matrix for principal component analysis were normalized, the combination coefficients satisfy the normalization condition [eqn. (7)],[20,21] where v represents

$$\xi_{\mathrm{C}1}\sum_{p=1}^{n} v_{1p} + \xi_{\mathrm{C}2}\sum_{p=1}^{n} v_{2p} = 1 \qquad (7)$$

elements of the eigenvectors. Therefore, among the two combination coefficients only one is independent. The independent combination coefficient can be determined by use of the known condition that the molar absorptivity of C_{84}–DEA complex at 568 nm is 7400 dm^3 mol^{-1} cm^{-1}. The pure absorption spectrum of the C_{84}–DEA complex thus obtained is also shown in Fig. 4. The surprisingly good agreement between the complex spectra determined by two different methods shows the self-consistency of the experimental data. The complex spectrum is broad, and has higher molar absorptivities

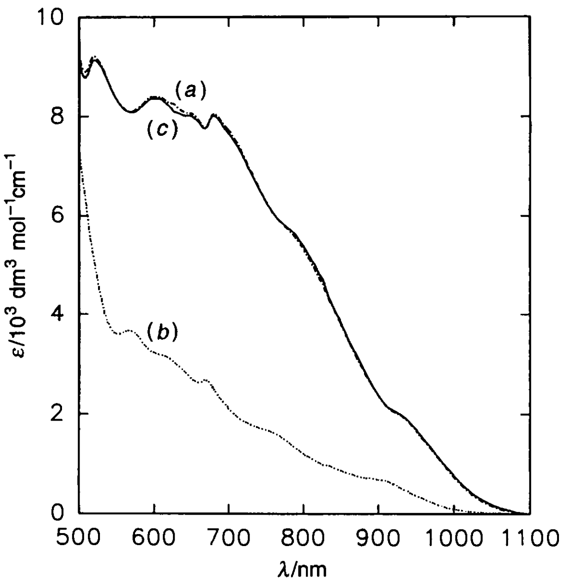

Fig. 4 Absorption spectra of (*a*) the C_{84} monomer and (*b*) C_{84}–DEA complex from Benesi–Hildebrand plots and (*c*) from principal component analysis

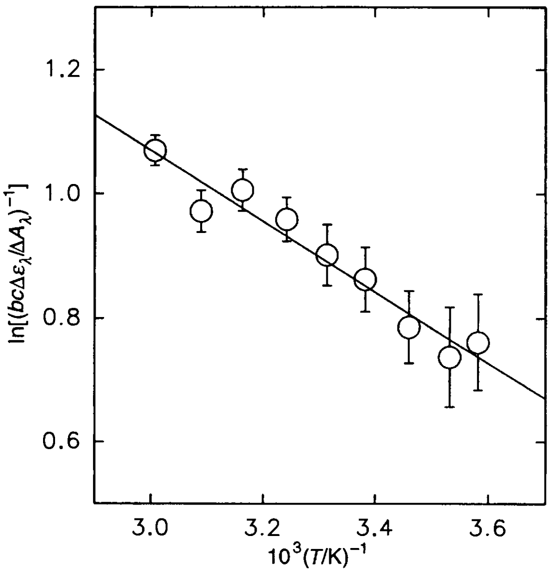

Fig. 5 A plot based on eqn. (9) for the temperature dependence of the C_{84}–DEA complex formation in neat DEA. The line is from a linear least-squares regression (slope = −571.8 and intercept = 2.79).

across the entire wavelength region under consideration (Fig. 4).

The C_{84}–DEA complex formation was also studied as a function of temperature from 6 to 60 °C in neat DEA. After correction for changes in solution concentration as a result of thermal expansion, the spectra are still somewhat temperature dependent. Observed absorbances decrease systematically with increasing temperature. The spectral changes can be attributed to a shift in the complex formation equilibrium with temperature because molar absorptivities of C_{84} in toluene are essentially temperature independent [eqn. (8)], where ΔH and

$$\ln K = -\Delta H/RT + \Delta S/R \qquad (8)$$

ΔS are enthalpy and entropy changes for the complex formation. A combination of eqns. (2) and (8) yields eqn. (9).

$$\ln[(bc\Delta\varepsilon_\lambda/\Delta A_\lambda) - 1] = \Delta H/RT - (\Delta S/R + \ln[\mathrm{DEA}]) \quad (9)$$

The fact that the right side of the equation is wavelength independent allows a global treatment of data at multiple wavelengths. A plot of eqn. (9) for data at 15 different wavelengths from 560 to 840 nm with a 20 nm interval is shown in Fig. 5. A linear least-squares regression (correlation coefficient 0.973) yields a ΔH value of −1.14 kcal $\mathrm{mol^{-1}}$ and a ΔS value of −9.17 cal $\mathrm{mol^{-1}\ K^{-1}}$, which are close to those of the C_{60} and C_{70} complexes.[25] The K value at room temperature obtained from $\exp(-\Delta G/RT)$ (0.069 $\mathrm{M^{-1}}$) is very close to that determined from the global Benesi–Hildebrand plot (Fig. 3), which also indicates that the experimental results and the data treatments are self-consistent.

Acknowledgements

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