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Complexation of Fullerene C_{60} with Various Aromatic Donors

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Abstract—Complexation of fullerene C_{60} with aromatic donors in CCl_4 and decalin was studied spectrophotometrically in the visible and near UV range, and the equilibrium constants were determined.

The chemistry of fullerenes as a new allotropic modification of carbon is one of the most actively developing branches of modern chemistry. The availability of fullerene C_{60} in macroscopic amounts allows preparation and study of its derivatives, in particular, molecular complexes.

The structure and chemical behavior of C_{60} were studied in numerous papers. Their results show that fullerene C_{60} is a polyunsaturated compound with π-acceptor properties. It stands out among other acceptor molecules owing to large size, spherical shape, unique electronic structure, high symmetry, and high polarizability; its polarizability exceeds several times that of other π-acceptor molecules. Therefore, polarization van der Waals forces play a significant role in formation of fullerene donor–acceptor complexes.

Compounds of the donor–acceptor type are formed when C_{60} is dissolved in various organic solvents. Most of the complexes with solvents are unstable, but in some cases C_{60} solvates can be isolated in the crystalline form [1].

We have studied the donor–acceptor interactions of fullerene C_{60} with naphthalene **I**, 1-methylnaphthalene **II**, 2-ethoxynaphthalene **III**, phenanthrene **IV**, *N,N*-dimethylaniline **V**, and *N,N*-diethylaniline **VI** in CCl_4 and with **II** in decalin. The interactions were monitored by electronic spectroscopy.

As compared to free fullerene C_{60}, the spectra of C_{60}–aromatic donor complexes exhibit stronger absorption in the range 390–410 nm, additional absorption at ~410 nm, and a charge-transfer band which can be revealed by subtracting the spectrum of C_{60} from the spectrum of the complex.

The new band with a maximum at ~410 nm apparently belongs to the carbon skeleton of C_{60}, since it is present in the spectra of many complexes, including complexes with transition metals, and also in CH_2C_{60} and $C_{60}O$. Complexation distorts the icosahedral structure, partially lifting the ban from forbidden transitions; as a result, the absorption becomes more intense [2].

Figure 1 shows the absorption spectra of fullerene C_{60}, a solution of fullerene C_{60} with *N,N*-diethylaniline in CCl_4, and the spectrum of the charge-transfer complex obtained by subtracting the spectrum of C_{60} from the spectrum of the mixture of C_{60} with *N,N*-diethylaniline.

In the case of strong donors such as **V**, **VI**, or **III**, the position of the charge-transfer band (λ_{max}) can be determined fairly accurately, whereas in the complexes with **I**, **II**, and **IV** it is partially obscured by the absorption of fullerene C_{60} and is manifested as a shoulder at 410–450 nm (Fig. 2).

In the case of still weaker donors (quinoline, 1-naphthyl methyl ketone), the charge-transfer band cannot be identified at all because of its strong short-wave shift.

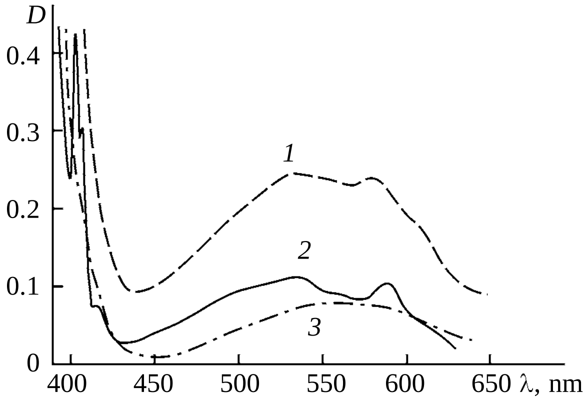

Fig. 1. Electronic absorption spectra of solutions of fullerene C_{60} and *N,N*-diethylaniline in CCl_4: (*1*) mixture of *N,N*-diethylaniline (*c* 1.27 M) and C_{60} (*c* 1.26×10^{-4} M), (*2*) fullerene C_{60} (*c* 1.26×10^{-4} M), and (*3*) spectrum of the charge-transfer complex obtained by subtracting spectrum *2* from spectrum *1*.

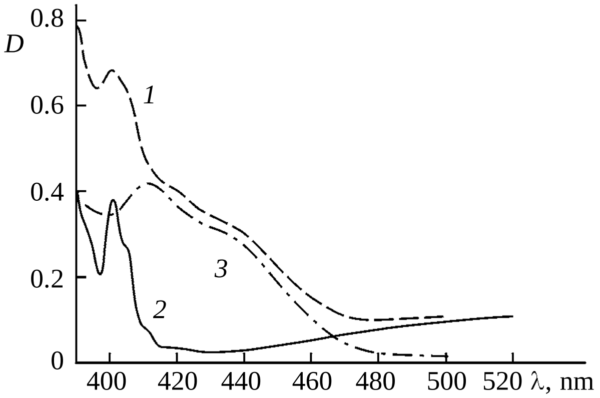

Fig. 2. Electronic absorption spectra of solutions of fullerene C_{60} and 1-methylnaphthalene in CCl_4: (*1*) mixture of 1-methylnaphthalene (*c* 1.02 M) with C_{60} (*c* 1.26×10^{-4} M), (*2*) fullerene C_{60} (*c* 1.26×10^{-4} M), and (*3*) spectrum of the charge-transfer complex obtained by subtracting spectrum *2* from spectrum *1*.

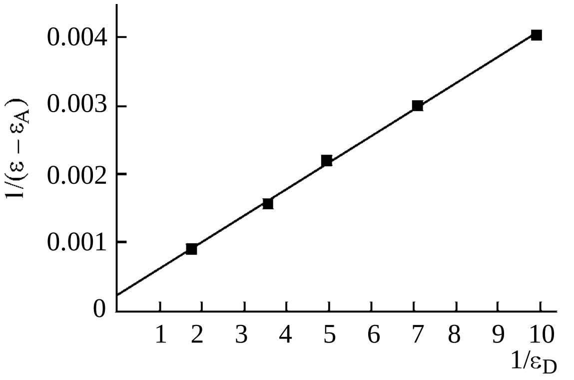

Fig. 3. Graphic representation of the Ketelaar equation for a solution of fullerene C_{60} and phenanthrene in CCl_4.

The formation constants of complexes are usually determined using the Benesi–Hildebrand equation; one of the components is taken in a large excess, and 1 : 1 complexation stoichiometry is presumed [3]:

$$\frac{lc_{\mathrm{f}}}{D_\lambda} = \frac{1}{\varepsilon_\lambda} + \frac{1}{K\varepsilon_\lambda}\left(\frac{1}{c_{\mathrm{D}}}\right),$$

where c_{f} is the fullerene C_{60} concentration; c_{D}, donor concentration; K, equilibrium constant; l, cell thickness; D_λ, optical density at the chosen wavelength; and ε_λ, extinction coefficient of the complex.

However, when one of the components of the complex absorbs at the analytical wavelength, the Ketelaar equation is used [4]:

$$\frac{1}{\varepsilon - \varepsilon_{\mathrm{A}}} = \frac{1}{Kc_{\mathrm{D}}(\varepsilon_{\mathrm{DA}} - \varepsilon_{\mathrm{A}})} + \frac{1}{\varepsilon_{\mathrm{DA}} - \varepsilon_{\mathrm{A}}},$$

where K is the equilibrium constant; c_{D}, donor concentration; ε_{A}, molar extinction coefficient of the acceptor; ε, measured molar extinction coefficient of the complex; and $\varepsilon_{\mathrm{DA}}$, true molar extinction coefficient of the complex.

The constants K obtained with the Ketelaar equation for **I**–**VI** in CCl_4 are as follows ($\lambda_{\max}$ of the charge-transfer band, nm, is given in parentheses): 0.68 (440), 0.58 (440), 0.65 (440), 0.62 (440), 0.65 (520), and 0.67 l mol^{-1} (560), respectively; for **II** in decalin, 0.61 l mol^{-1} (440). The optical density used in the calculations was taken at a maximum of the charge-transfer band. For quinoline and 1-naphthyl methyl ketone, the constants were not calculated, since we failed to localize accurately the charge-transfer band in the spectra of the corresponding complexes.

The plots obtained in calculations of the complexation constants were virtually linear (Fig. 3), which suggests formation of 1 : 1 complexes.

Our results show that the constants of formation of 1 : 1 fullerene–π donor complexes vary within 0.58–0.68. Previously the complexation constants with C_{60} were determined for **V** in toluene (*K* 0.28) [5] and for **V**, **VI**, and some other anilines in chlorobenzene (*K* 0.29–0.61) [6]. Neither we nor other authors revealed any correlation between the complexation constants and structure of the donor molecule.

EXPERIMENTAL

The electronic absorption spectra of solutions of fullerene C_{60} and aromatic donors were recorded on an SF-26 spectrophotometer in quartz cells (*l* 1 cm) against pure solvent. The fullerene C_{60} concentration in solutions was $\sim 1.2 \times 10^{-4}$ M, and the concentration of donors was varied within 0.05–2 M. All the measurements were performed at 20 ± 2°C.

Fullerene C_{60} (99.5%) was purchased from Merck. CCl_4 was purified by shaking with aqueous NaOH followed by distillation, and decalin, by shaking with sulfuric acid followed by distillation at reduced pressure.

1-Methylnaphthalene, quinoline, 1-methyl naphthyl ketone, and aniline were purified by distillation at reduced pressure. Phenanthrene was recrystallized from isooctane–toluene, and 2-ethoxynaphthalene was recrystallized twice from isooctane.

REFERENCES

1. Konarev, D.V. and Lyubovskaya, R.N., *Usp. Khim.*, 1999, vol. 50, no. 1, p. 23.

2. Gorel’skii, S.I., Magdesieva, T.V., and Butin, K.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, no. 6, p. 1453.
3. Andrews, L.J. and Keefer, R.M., *Molecular Complexes in Organic Chemistry*, San Francisco: Holden-Day, 1964. Translated under the title *Molekulyarnye kompleksy v organicheskoi khimii*, Moscow: Mir, 1967, p. 101.
4. Sverdlova, O.V., *Elektronnye spektry v organicheskoi khimii* (Electronic Spectra in Organic Chemistry), Leningrad: Khimiya, 1985, p. 202.
5. Sibley, S.P., Campbell, R.L., and Silber, H.B., *J. Phys. Chem.*, 1995, vol. 99, no. 15, p. 5274.
6. Nadtochenko, V.A., Denisov, N.N., and Levin, P.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1995, no. 6, p. 1078.