Interaction of fullerene C_{60} with iodine in organic solvents

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The interaction of fullerene C_{60} with molecular iodine in organic solvents was studied. The stoichiometry of the complex formed, $C_{60} : I_2 = 1 : 3$, was determined spectrophotometrically and by the interphase distribution technique. The constant of the formation of the adduct in toluene was calculated to be $\log K = 8.9 \pm 0.3$.

Key words: fullerenes, iodine.

The study of the complexation of fullerenes with organic ligands and inorganic compounds in solutions is very important for the development of the chemistry of fullerenes. The use of homogeneous media for conducting the reactions is a very promising approach for the preparative synthesis of fullerene compounds.

Many works have dealt with the interaction of fullerenes with halogens.[1,2] For some time, it was considered that iodine does not add to the fullerene molecule due to the high ionization potential of C_{60}, which equals 7.6 eV.[3] However, it has been shown[4] that heating to 130 °C for 24 h with a large excess of iodine affords a compound with $C_{60}I_2$ stoichiometry. In addition, the formation of this compound requires photodissociation of the iodine molecule into two radicals under Hg-irradiation, that is, iodine is in the atomic form rather than the molecular form in the complex obtained.[4]

The present work examines the interaction of molecular iodine with fullerene C_{60} in organic solvents.

Experimental

The samples of fullerene C_{60} were isolated from graphite black and purified by chromatography.[5] The content of C_{60} in the samples was 99.7±0.1 %. The absorption spectra were recorded on a Specord UV VIS spectrophotometer. The concentrations of iodine and fullerene C_{60} were determined photometrically.

The experiments on the interphase distribution of iodine were carried out in test tubes with ground stoppers at 20±2 °C and at a phase volume ratio of 1 : 1. The samples were stirred at 60 r.p.m. for 1 h, which is sufficient for the attainment of equilibrium in the system.

Results and Discussion

The addition of iodine to a solution of fullerene C_{60} results in a change in the solution color indicating that a reaction has occurred. Using the spectrophotometric isomolar series method (Fig. 1), we determined the ratio of the components in the complex formed to be $C_{60} : I_2 = 1 : 3$. This complex is more hydrophobic than iodine and, therefore, the partition coefficient of iodine (D) between the aqueous and organic phases increases when fullerene C_{60} is introduced into a solution of iodine in toluene. (Fig. 2, *a*). This allowed us to use the method of distribution of iodine between the aqueous and organic phases in the presence of fullerene for studying the complexation of fullerene C_{60} with iodine.

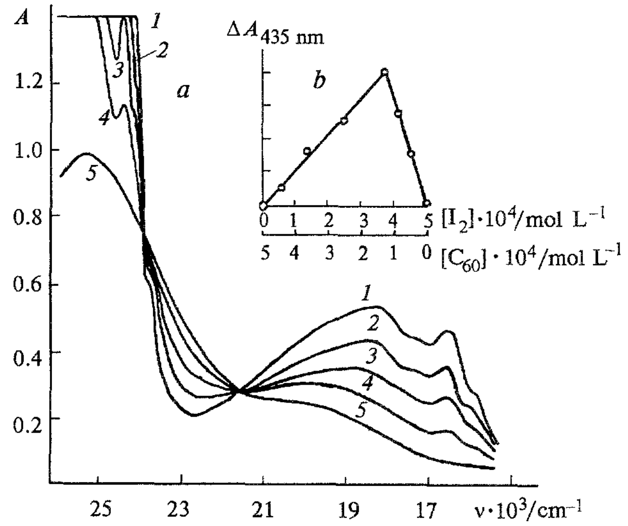

Fig. 1. *a.* Absorption spectra of $5 \cdot 10^{-4}$ *M* solutions of fullerene C_{60} (*1*), iodine (*5*), and their isomolar mixtures (*2—4*) in toluene. Concentration of fullerene C_{60}/mol L^{-1}: *2*, $1.25 \cdot 10^{-4}$; *3*, $2.5 \cdot 10^{-4}$; *4*, $3.75 \cdot 10^{-4}$; concentration of iodine/mol L^{-1}: *2*, $3.75 \cdot 10^{-4}$; *3*, $2.5 \cdot 10^{-4}$; *4*, $1.25 \cdot 10^{-4}$. *b.* Isomolar diagram of the change in optical density of the solution, $\Delta A_{435\ nm} = A - (C_{C60} \cdot \varepsilon_{C60} + C_{I2} \cdot \varepsilon_{I2})$.

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If the formation of the adduct of iodine with fullerene C_{60} in the organic phase occurs according to the reaction

$$C_{60} + nI_2 \rightleftharpoons C_{60} \cdot nI_2 ,$$

the constant of the formation of the complex is

$$K = \frac{[C_{60} \cdot nI_2]}{[C_{60}][I_2]^n} ,$$

where n is the stoichiometric coefficient, and $[C_{60} \cdot nI_2]$, $[C_{60}]$, and $[I_2]$ are the equilibrium concentrations of the adduct, fullerene, and iodine, respectively, then the partition coefficient of iodine between the aqueous and organic phases can be expressed as

$$D = \frac{[I_2]_{org} + [C_{60} \cdot nI_2]_{org}}{[I_2]_{aq}} = \frac{[I_2]_{org} + K[C_{60}]_{org}[I_2]^n_{org}}{[I_2]_{aq}} =$$

$$= \frac{[I_2]_{org}(1 + K[C_{60}]_{org}[I_2]^{n-1})_{org}}{[I_2]_{aq}} =$$

$$= D_0(1 + K[C_{60}]_{org}[I_2]^{n-1}),$$

D_0 is the partition coefficient of iodine in the absence of fullerene C_{60} in the organic phase, and the indices "org" and "aq" refer to the organic and aqueous phases, respectively.

The dependence of the partition coefficient of iodine on the concentration of fullerene C_{60} and iodine in the organic phase permits us to determine the stoichiometric coefficient n and the constant of the formation of the complex of fullerene C_{60} with iodine according to the equation

$$\log(D/D_0-1) = \log K + \log[C_{60}]_{org} + (n-1)\log[I_2]_{org}$$

As can be seen from Fig. 2 *b*, the slope of the plot $\log(D/D_0-1) = f(\log[I_2]_{org})$ is 2, which corresponds to the stoichiometric coefficient $n = 3$. These data coincide with the results of the spectrophotometric determination of the composition of the complex. Using the least-squares method, the constant of the formation of the complex $C_{60} \cdot 3I_2$ was determined to be $\log K = 8.9 \pm 0.3$.

The formation of the adduct of iodine with fullerene C_{60} also occurs in other organic solvents (benzene, *o*-xylene, chloroform, and hexane).

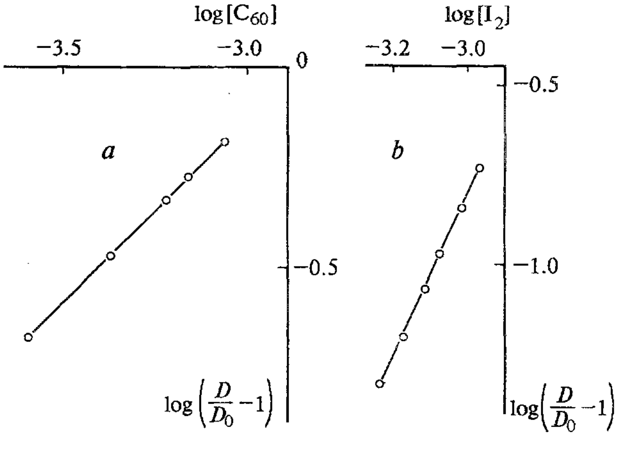

Fig. 2. Plot of the partition coefficient of iodine between a 0.1 *M* solution of KI and toluene *vs* concentration of fullerene C_{60} (*a*) and iodine (*b*) in the organic phase.

Table 1. Dependence of the solubility of fullerene C_{60} in chloroform on the concentration of iodine

[I] / mol L^{-1}	*S* / mg mL^{-1}	[I] / mol L^{-1}	*S* / mg mL^{-1}
0	0.16	$5.0 \cdot 10^{-3}$	0.36
$5.0 \cdot 10^{-4}$	0.17	$1.0 \cdot 10^{-2}$	0.65
$2.5 \cdot 10^{-3}$	0.22	$2.5 \cdot 10^{-2}$	2.60

Note. [I] is the concentration of iodine; *S* is the solubility of fullerene C_{60}.

It is known that the constant of the interphase distribution of a complex is proportional to its solubility in the organic solvent. Therefore, taking into account the constant of the formation of the complex of fullerene with molecular iodine, one should predict a noticeable increase in the solubility of fullerene in the solvent in the presence of iodine. In fact, the data of Table 1 show that the solubility of fullerene C_{60} increases as the iodine concentration increases.

When these solutions come into contact with aqueous solutions of potassium iodide, iodide passes into the aqueous phase, and the excess fullerene precipitates. This phenomenon can be used to increase the efficiency of the extraction of fullerenes from graphite black by organic solvents.

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