QUANTITATIVE ANALYSIS OF C_{60} AND C_{70} FULLERENE SOLUTIONS BY SPECTROPHOTOMETRIC METHOD

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Introduction

Optimization of the technique for preparation, extraction and separation of fullerenes largely depends on the analytic provision. The absorption spectrophotometric method, being rather precise, fast and accessible method for quantitative analysis, is not widely applied mainly due to the absence of exact values of molar absorption factors (MAF) for C_{60} and C_{70} solutions.

According to [1-23], optical density of fullerene solutions obeys Beer's law, i.e. it shows an additive property what gives possibility to evaluate C_{60} and C_{70} concentrations in solutions of their mixtures by solving the systems of two linear equations:

$$\begin{cases} A_1 = \varepsilon_{60}^1 \cdot X + \varepsilon_{70}^1 \cdot Y \\ A_2 = \varepsilon_{60}^2 \cdot X + \varepsilon_{70}^2 \cdot Y \end{cases} \qquad (1)$$

where A_1 and A_2 - optical densities of the solution studied for λ_1 and λ_2 waves, respectively;
ε_{60}^1 and ε_{60}^2 - MAF of the C_{60} solution for λ_1 and λ_2 wave-lengths;
ε_{70}^1 and ε_{70}^2 - MAF of the C_{70} solution for λ_1 and λ_2 wave-lengths;
X and Y - mole concentrations of C_{60} and C_{70} in the solution studied.

The comprehensive analysis of errors of photometric methods demonstrated that the highest accuracy of measurements was achieved in the solutions which absorption capability equals about 63% [2].

The concentrations of these solutions are easily determined using S-shaped plots for the dependence of intensity of the passing beam *P* on logarithm of the solution concentraion *C*. The most exact measurements are performed in the range of concentrations where the equation

$$\frac{\frac{dP}{dC}}{C} = \frac{dP}{d\ln C} = 0{,}434\frac{dP}{d\lg C} \qquad (2)$$

takes the maximum value, i.e. in the inflection point in the S-shaped curve. The part of the points in the S-shaped curve is usually in the tangent to this curve in the inflection point. These points determine the concentraion range in which accuracy of measurements of optical density is still rather high.

Experimental

Fullerenes extracted by toluene from the fullerene-containing soot have been studied. The soot was prepared by the electric arc method.

The extract was separated into C_{60} and C_{70} during several cycles in the chromatographic column with graphite filler of the given size.

Fullerene extraction and crystallization were carried out at room temperature in order to decrease the residual amount of toluene [3]. The crystals produced were washed with diethyl ether and kept under vacuum for 36-48 h. Then the crystals were used to prepare solutions which concentrations were calculated considering the residual amount of toluene present in crystallosolvates.

Absorption spectra were taken in 10.01 optical cells on CF-26 spectrophotometer with the range of wave-lengths from 2 to 5 nm and with the digital output.
Fullerenes solutions were protected from the light beams.
99 absorption spectra for C_{60}, C_{70} solutions and their mixtures have been measured and analyzed.

Results and discussion

In the work presented the molar absorption factors, ε_{60} and ε_{70}, of pure C_{60} and C_{70} solutions for each wave-length have been calculated using the equation

$$\varepsilon_{60}\,(\varepsilon_{70}) = \frac{0.434}{C_{I.P.}} \qquad (3)$$

where C_{IP} - C_{60} (C_{70}) fullerene concentration corresponding to the inflection point in the plot $P = f(\lg C)$.

Table 1. Molecular absorption factors of C_{60} and C_{70} in toluene

λ , nm	ε_{60}	ε_{70}
356,3	22894	—
365,2	15630	—
372,0	11722	—
383	—	—
407	3136	14371
418,4	1054	13108
439	334	15049
472,8	607	21506
540	933	9604

Values of MAF calculated for C_{60} and C_{70} toluene solutions and corresponding wave-lengths are given in Table 1.

The values of MAFattained for C_{60} and C_{70} toluene solutions have been used to calculate individual concentrations of C_{60} and C_{70} in the solutions of their mixtures using Eq.(1) and optical parameters of absorption spectra measured in the spectral range from 340 nm to 650 nm.

Numerous calculations indicate that the most exact results are obtained in the solutions which optical densities are in the range from 0.3 to 0.7 relative unit. Table 2 shows values of optimum concentrations for solutions of the fullerene mixture and corresponding ranges of analytical wave-lengths.

Fig. 1 shows the change of optical density in the mixture solutions with changing concentrations. The thickened lines mark the sections in the spertra which are in the analytic range of wave-lengths. As seen in Fig.1, the analytical range of wave-lengths expands and shifts to the long wave region.

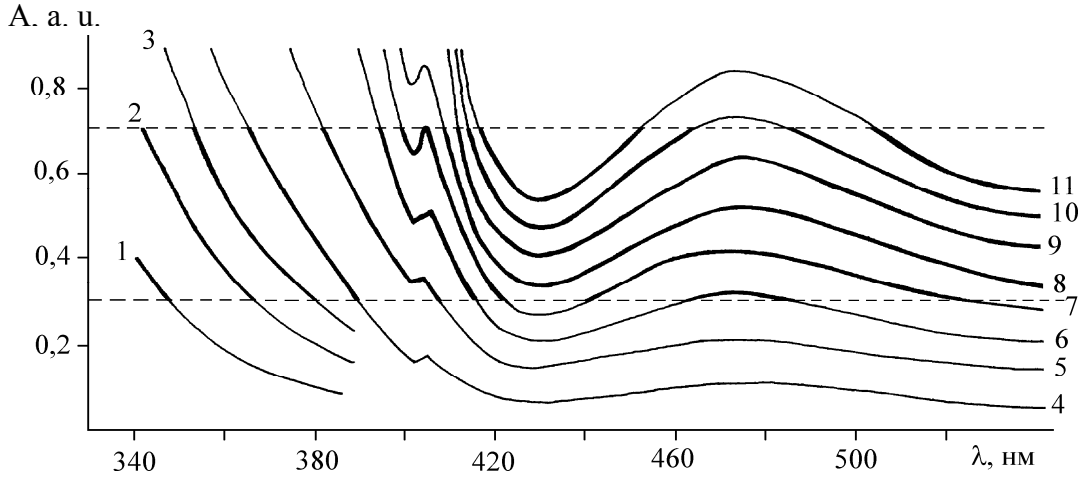

Fig.1. Spectra for solutions of C_{60} and C_{70} fullerene mixtures; concentrations of solutions 1-11 are given in Table 2.

Table 2. Optimum concentrations of fullerenes and corresponding ranges of wave-lengths

N спектра	C, г/л	Интервал аналитических длин волн, нм
1	0,0065	340 – 350
2	0,0129	340 – 370
3	0,0194	350 – 380
4	0,0324	365 – 390
5	0,0647	385 – 410
6	0,0971	395 – 416 450 – 495
7	0,1294	400 – 540
8	0,1618	410 – 550
9	0,1942	410 – 570
10	0,2265	415 – 560
11	0,2589	418 – 450 510 – 600

Conclusions

1. MAF for toluene solutions of C_{60} and C_{70} fullerenes have been evaluated.
2. The ranges of wave-lengths and fullerene concentrations have been determined. In these ranges one can obtain the most exact results (±1%) of quantitative analysis of fullerene solutions by spectrophotometric method.

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