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Synthesis and Identification of Bromofullerenes $C_{70}Br_8$ and $C_{70}Br_{10}$ and Their Solubility in Some Aromatic Solvents

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Abstract—Bromofullerenes $C_{70}Br_8$ and $C_{70}Br_{10}$ were synthesized and identified by electronic absorption and infrared spectroscopy. Their solubility in aromatic solvents (benzene, toluene, *o*-xylene, and *o*-dichlorobenzene) was studied in the temperature range from 20 to 60°C.

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A fairly large number of methods for the synthesis and identification of lower fullerenes C_{60} and C_{70} have been reported [1, 2]. The solubility of C_{60} and C_{70} in various solvents (including polythermal conditions) was also the subject of many publications [1, 3, 4]. Much less attention was given to the synthesis and identification of derivatives of C_{60} and C_{70}, in particular bromo derivatives like C_nBr_m (n = 60, 70; m = 6, 8, 10, 24). The solubility of brominated C_{60} derivatives was studied in various individual organic solvents [3, 4, 8–10], as well as in water–alcohol mixtures [12], at different temperatures. We have found no published data on the solubility of brominated C_{70} derivatives. The goal of the present study was to synthesize and identify bromofullerenes $C_{70}Br_8$ and $C_{70}Br_{10}$ by electronic absorption and IR spectroscopy, as well as to estimate their solubility in aromatic solvents (benzene, toluene, *o*-xylene, *o*-dichlorobenzene) in the temperature range from 20 to 60°C (see table).

The starting compound was fullerene C_{70} with a purity of 99.5 wt % (manufactured at the "Innovations of Leningrad Institutes and Enterprises" Closed Corporation, St. Petersburg); it contained 0.5 wt % of C_{60} as the major impurity. The synthesis of $C_{70}Br_8$ was performed according to the procedure proposed in [12]. A mixture of 200 mg of C_{70} and 10 ml of Br_2 was stirred for 4–5 min at room temperature using a magnetic stirrer. Excess bromine was distilled off from the resulting homogeneous solution under reduced pressure (15 mm) to isolate 1:2 bromine solvate $C_{70}Br_8 \cdot 2Br_2$ as a black crystalline material. The product was dried at 70°C (~15 mm) to decompose the solvate; the yield of $C_{70}Br_8$ was 73%.

To synthesize $C_{70}Br_{10}$, a mixture of 200 mg of C_{70} and 10 ml of Br_2 was stirred for 48 h at room temperature using a magnetic stirrer. Removal of excess bromine under reduced pressure (15 mm) afforded lemon yellow 1:1 solvate $C_{70}Br_{10} \cdot Br_2$ in quantitative

Solubility of bromofullerenes $C_{70}Br_n$ (g/l) in aromatic solvents in the temperature range from 20 to 60°C

Temperature, °C	Benzene	Toluene	*o*-Xylene	*o*-Dichlorobenzene
		$C_{70}Br_8$		
20	3.89	5.45	9.99	20.7
40	4.67	7.01	11.8	21.9
60	5.45	8.17	13.6	29.1
		$C_{70}Br_{10}$		
20	1.29	0.086	3.53	8.06
40	2.24	0.431	3.88	10.4
60	2.93	2.24	4.22	22.3

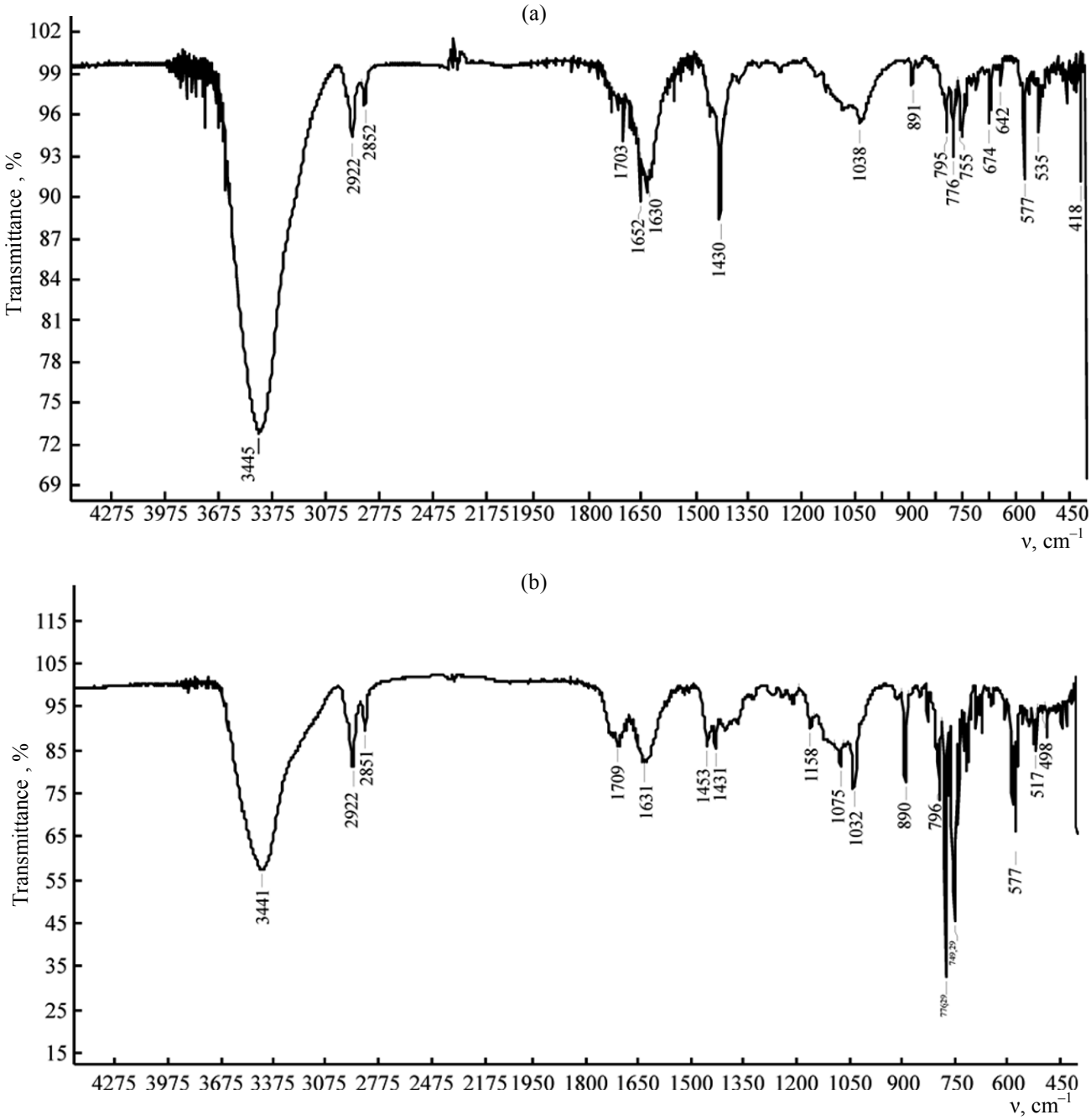

Fig. 1. IR spectra of (a) $C_{70}Br_8$ and (b) $C_{70}Br_{10}$.

yield. The product was dried at 70°C (15 mm) to decompose the solvate; the yield of $C_{70}Br_{10}$ was 91%.

The IR spectra of solid samples of $C_{70}Br_n$ (n = 8, 10) in KBr were recorded on a Shimadzu FTIR-8400S spectrometer (Fig. 1). The spectral patterns in the low-frequency range (450–1050 cm^{-1}) were in a good agreement with published data [12]. The absorption of both bromo derivatives in that spectral region was characterized by similar frequencies but different intensities. Clearly defined triplets were observed at 795/776/755 cm^{-1} for $C_{70}Br_8$ and 796/776/749 cm^{-1} for $C_{70}Br_{10}$. The same applies to the characteristic peaks of $C_{70}Br_8$ at 577±3, 672±3, and 1035±5 cm^{-1}.

Electronic absorption spectra. Figure 2 shows the electronic absorption spectra of $C_{70}Br_n$ (n = 8, 10) in some aromatic solvents (*o*-xylene, *o*-dichlorobenzene,

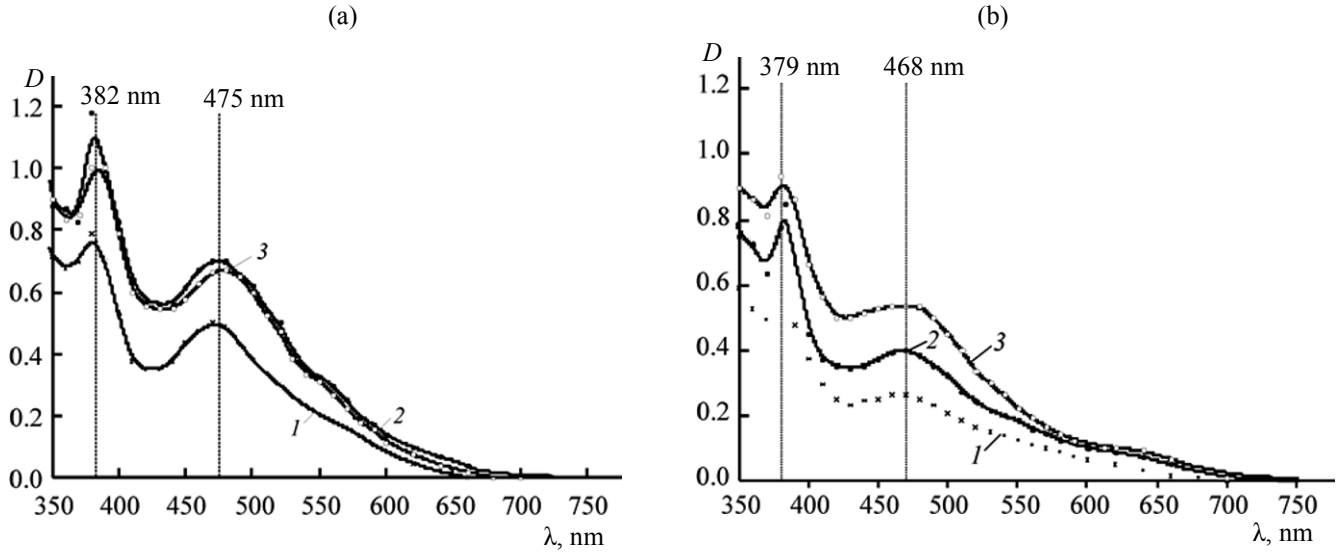

Fig. 2. Electronic absorption spectra of (a) $C_{70}Br_8$ and (b) $C_{70}Br_{10}$ in (*1*) *o*-xylene, (*2*) *o*-dichlorobenzene, and (*3*) α-chloronaphthalene.

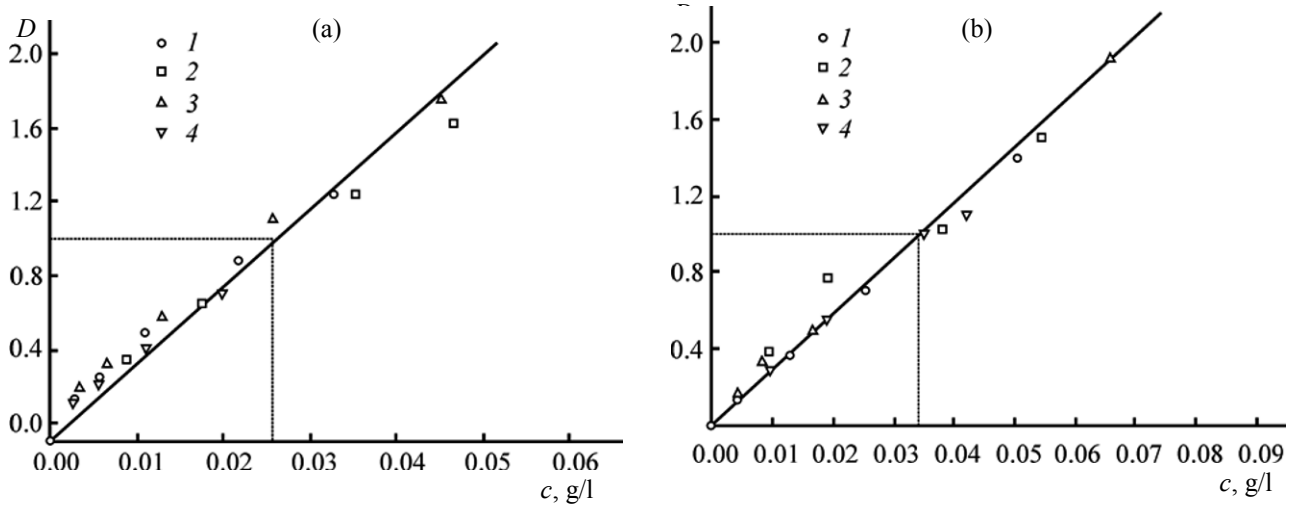

Fig. 3. Concentration dependences of the optical density at λ 379 nm of solutions of (a) $C_{70}Br_8$ and (b) $C_{70}Br_{10}$ in (*1*) *o*-xylene, (*2*) *o*-dichlorobenzene, (*3*) α-chloronaphthalene, and (*4*) benzene.

α-chloronaphthalene). Solutions of both bromofullerenes $C_{70}Br_n$ in all the examined solvents displayed in the near UV region well defined absorption bands with λ_{max} 379±4 and 373±6 nm, the absorption maxima of $C_{70}Br_{10}$ being slightly displaced to the blue region. Concentration dependences of the optical density at λ 379 nm for solutions in the above listed solvents and benzene were plotted to check whether the Beer–Lambert law is fulfilled. We propose the following equations for the calculation of $C_{70}Br_n$ concentration in any solvent:

$$c(C_{70}Br_8) = 0.0257\, D_{379}; \quad (1)$$

$$c(C_{70}Br_{10}) = 0.041\, D_{379}. \quad (2)$$

Here, $c(C_{70}Br_n)$ is the concentration of $C_{70}Br_n$ (g/l), D_{379} is the optical density of a solution of $C_{70}Br_n$ at λ 379±4 and a cell path length l of 1 cm. The concentration dependences of the optical density of $C_{70}Br_n$ solutions are shown in Fig. 3. It is seen that the Beer–Lambert law is fulfilled throughout the examined concentration range; therefore, formulas (1) and (2) are valid.

The temperature dependences of the solubility of bromofullerenes $C_{70}Br_n$ (n = 8, 10) were studied by the isothermal saturation method. For this purpose, a suspension of $C_{70}Br_n$ (n = 8, 10) in benzene, toluene, *o*-xylene, or *o*-dichlorobenzene (300 mg of a substrate in 10 ml of a solvent) was shaken for 10 h at a required temperature (20, 40, or 60°C) maintained with an

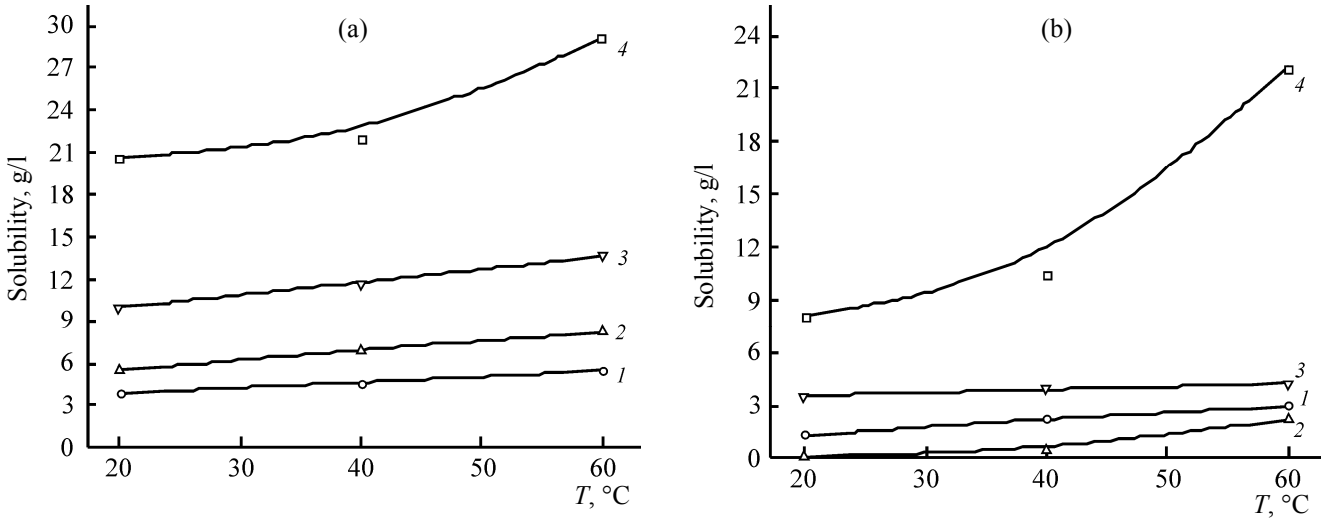

Fig. 4. Temperature dependences of the solubilities of (a) $C_{70}Br_8$ and (b) $C_{70}Br_{10}$ in (*1*) benzene, (*2*) toluene, (*3*) *o*-xylene, and (*4*) *o*-dichlorobenzene.

accuracy of ±0.05°C; the concentration of $C_{70}Br_n$ (n = 8, 10) was then determined by spectrophotometry at λ 379 nm using a Specord-32 instrument.

Figure 4 shows the temperature dependences of the solubilities of $C_{70}Br_n$ (n = 8, 10) in benzene, toluene, *o*-xylene, and *o*-dichlorobenzene in the temperature range from 20 to 60°C. Bromofullerenes $C_{70}Br_n$ are relatively readily soluble in the examined aromatic solvents, and their solubility monotonically increases as the temperature rises. The solubility of $C_{70}Br_8$ considerably increases in the series benzene < toluene < *o*-xylene < *o*-dichlorobenzene, and the corresponding solubility series for $C_{70}Br_{10}$ is toluene < benzene < *o*-xylene < *o*-dichlorobenzene. The solubility of $C_{70}Br_{10}$ in all the above solvents is appreciably higher than that of $C_{70}Br_8$.

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