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C_{60} – C_{70} – $C_6H_5CH_3$ Crystal Solvates: Structure and Thermal Stability

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Abstract—Differential scanning calorimetry (DSC) and X-ray diffraction were used to study the thermal stability and structure of C_{60} – C_{70} – $C_6H_5CH_3$ crystal solvates synthesized at room temperature. The decomposition of the crystal solvates generates C_{60} – C_{70} solid solutions with hexagonal close-packed (hcp) structure.

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Fullerenes in the condensed state extracted from fullerene black retain some amount of the solvent. Solvent molecules can reside both on the facets of fullerenes [1] and, as clathrates/crystal solvates, in interstices of van der Waals lattices built of fullerenes [2]. These solvates are supposed to be responsible for the non-monotonic behavior of C_{60} solubility in some organic solvents [3], this nonmonotonicity being important for the separation of fullerene mixtures.

The extraction of fullerenes by a boiling solvent and the slow evaporation of fullerene solutions at room temperature can generate crystal solvates, whose molecular composition and structure have been studied insufficiently. The systems of several types of fullerenes, in particular, in C_{60} – C_{70} –solvent systems, can generate complex mixed solvates or solid solutions of solvates. Solvates of the C_{60} – C_{70} – o - $C_6H_5(CH_3)_2$ ternary system form a solid solution, which is isomorphic to the $C_{60} \cdot 2(o$ - $C_6H_4(CH_3)_2$) solvate [4, 5]. The structural alteration of mixtures after the solvent is removed during heat treatment is not discussed in the above-cited works. However, the formation of fullerene C_{60}/C_{70} solid solutions is quite possible as a result of the thermally activated demixing of mixed crystal solvates. The similarity of the molecular sizes of fullerenes C_{60} and C_{70} implies the possibility of the existence of substitutional solid solutions of C_{60} in C_{70} and of C_{70} in C_{60} with face-centered cubic (fcc) and/or hexagonal close-packed (hcp) lattices [6, 7]. Complete miscibility was found in vacuum-sublimed samples [7], and incomplete miscibility was found in a sample prepared from solutions [7, 8].

The C_{60} –toluene (C_{60} – $C_6H_5CH_3$) system forms two types of monoclinic crystal solvates $C_{60} \cdot 2C_6H_5CH_3$ (I, $C2/m$, $a = 17.03(2)$ Å, $b = 10.344(4)$ Å, $c = 11.16(1)$ Å, $\beta = 107.10(7)^\circ$) and $C_{60} \cdot C_6H_5CH_3$ (II, $a = 10.25(3)$ Å, $b = 31.3(1)$ Å, $c = 10.17(4)$ Å, $\beta = 94.0(3)^\circ$) [9]. Solvate I is metastable and melts incongruently at 12°C to yield

a saturated solution of C_{60} in toluene and solvate II, which decomposes into C_{60} and toluene at $\sim 48^\circ\text{C}$ [10]. The orthorhombic C_{60} –toluene (1 : 1) solvate was prepared experimentally [11] with the following parameters: $a = 10.37$ Å, $b = 31.67$ Å, $c = 10.13$ Å.

For the C_{70} –toluene system, the $C_{70} \cdot C_6H_5CH_3$ solvate is known with orthorhombic structure (space group $Am\bar{m}2$) and the unit cell parameters $a = 10.86(2)$ Å, $b = 10.55(6)$ Å, $c = 33.09(8)$ Å [12, 13]. Data on its thermal stability are few. The endotherm at 130 – 180°C observed on the differential scanning calorimetry (DSC) curve for a toluene-containing sample is associated with the decomposition of the crystal solvate [14].

It is known [15] that monoclinic $C_{60} \cdot C_6H_5CH_3$ and orthorhombic $C_{70} \cdot C_6H_5CH_3$ solvates are quasi-isomorphic to the orthorhombic n -pentane solvate of C_{60} (1 : 1) [16]. From the quasi-isomorphism of $C_{60} \cdot C_6H_5CH_3$ and $C_{70} \cdot C_6H_5CH_3$, we can suggest the existence of mixed solvates (solid solutions) in the C_{60} – C_{70} – $C_6H_5CH_3$ system at room temperature; their suggested composition is $(C_{60})_x(C_{70})_{1-x} \cdot C_6H_5CH_3$.

EXPERIMENTAL

Here, we studied the structure and thermal stability of crystal solvates of the C_{60} – C_{70} – $C_6H_5CH_3$ system containing 0, 1.9, 4.8, 10, 15, 20, 30, 50, and $100 (\pm 0.3)$ wt % C_{70} in the C_{60}/C_{70} starting mixture using DSC and X-ray diffraction. To prepare test samples, weighed samples of references C_{60} (99.95%) and C_{70} (98%) were mixed and completely dissolved in toluene (high-purity grade). Then, the solution was allowed to concentrate until dry at room temperature (for ~ 24 h). X-ray diffraction was measured on DRON-6 using $\text{CuK}\alpha$ radiation in the angle range 5° – 40° . DSC curves were recorded on PerkinElmer Diamond DSC in aluminum crucibles under heating from -50 to 220°C at 20 K/min in flowing argon.

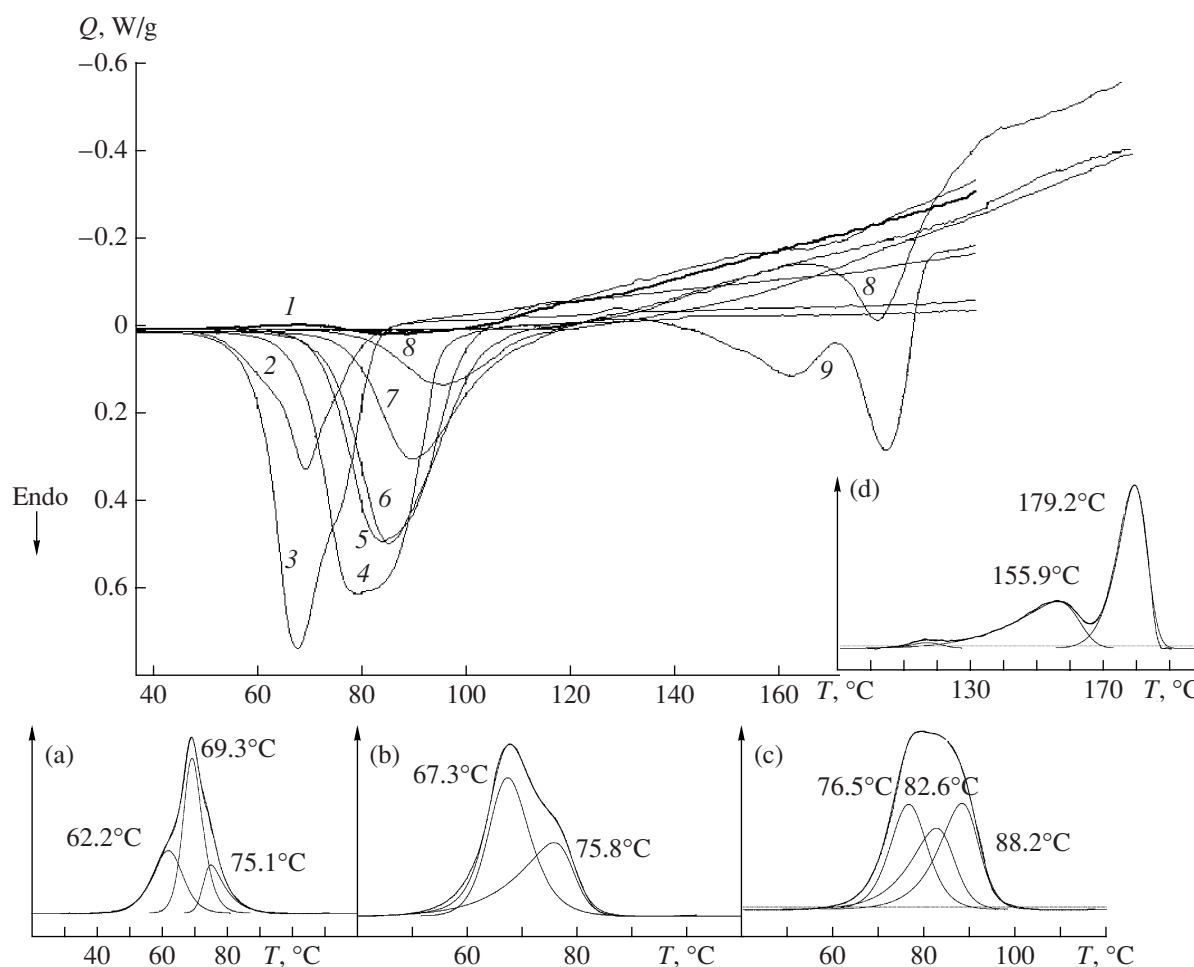


Fig. 1. DSC curves for initially prepared C_{60} - C_{70} - $C_6H_5CH_3$ samples containing (1) 0, (2) 1.9, (3) 4.8, (4) 10, (5) 15, (6) 20, (7) 30, (8) 50, and (9) 100 wt % C_{70} in C_{60}/C_{70} mixtures. Q is heat flow. The insets in the lower part of Fig. 1 are fragments of DSC curves for initially prepared C_{60} - C_{70} - $C_6H_5CH_3$ samples containing (a) 1.9, (b) 4.8, (c) 10, and (d) 100 wt % C_{70} in C_{60}/C_{70} mixtures. Endotherms are counted from bottom up.

Figure 1 illustrates the results of DSC measurements for C_{60} - C_{70} - $C_6H_5CH_3$ samples with various C_{60}/C_{70} proportions. Let us start with the C_{60} - $C_6H_5CH_3$ and C_{70} - $C_6H_5CH_3$ binary systems. The heat flow versus temperature curve for the C_{60} -toluene system (Fig. 1, curve 1) has a small, broad endotherm at $\sim 89^\circ\text{C}$, apparently associated with the incongruent melting of $C_{60} \cdot C_6H_5CH_3$ [10]. This sample being prepared at room temperature, it is free of $C_{60} \cdot 2C_6H_5CH_3$, whose decomposition temperature is $\sim 12^\circ\text{C}$ [10]. The endotherm temperatures and relevant heats for all test samples are listed in the table.

Figure 2 displays X-ray diffraction patterns for an initially prepared C_{60} -toluene sample and for the same samples after heating to certain temperatures previously determined from the DSC curve. To avoid oxidation, all samples were thermally treated in dynamic vacuum ($\sim 10^{-4}$ mmHg) at 20 K/min. Data analysis shows that the initially prepared samples consist of fcc fullerite C_{60} with $a = 14.187 \pm 0.10$ Å

(Cf. $a = 14.17$ Å [17]) and the monoclinic crystal solvate with $a = 10.38 \pm 0.02$ Å, $b = 32.77 \pm 0.02$ Å, $c = 10.25 \pm 0.01$ Å, $\beta = 90.6^\circ \pm 0.2^\circ$. With account for the intensities of the solvate and fullerite lines, this X-ray diffraction pattern corresponds to fcc C_{60} concentrations within 1–10%. The appearance of fcc fullerite in the phase composition of this sample is likely due to the high solvent evaporation rate during sample preparation.

Heating to 60°C increases the diffraction intensities from the fcc fullerite and decreases those from the solvate (Fig. 2). The solvate lines completely disappear upon heating to 109°C , signifying its decomposition in agreement with data in [10] and DSC results (Fig. 1). X-ray diffraction pattern 3 in Fig. 2 shows two phases in the sample. Along with the rather narrow and strong lines of fcc fullerite C_{60} ($a = 14.187 \pm 0.010$ Å), broad peaks characteristic of hcp fullerite C_{60} [18] are observed in this X-ray diffraction pattern. The considerable line width can arise from high imperfection of this phase and/or very small crystallite size. The lines of

the hcp phase have noticeably lower intensities than the fcc phase, and its fraction in the sample can reach 50–80% [19]. Presumably, hcp fullerite C₆₀ is generated by the decomposition of the crystal solvate. Hexagonal close-packed C₆₀ was also observed in samples prepared by salting out and cryoextraction [18]. Samples retain this structural state after 2-h annealing at 200–400°C.

For the C₇₀-toluene system, the DSC curve (Fig. 1, curve 9) shows two endotherms at 156 and 179°C (see Fig. 1d). The formation of orthorhombic C₇₀ · C₆H₅CH₃ is discussed in [12, 13], but kinetic data on its decomposition are absent. The DSC curve implies either the possibility of existence of one more solvate in this system under the specified sample-preparation conditions or the two-stage decomposition of C₇₀ · C₆H₅CH₃.

Figure 3 displays X-ray diffraction patterns for an initially prepared C₇₀-C₆H₅CH₃ sample and after heating. The initially prepared sample contains lines from the crystal solvate exclusively and does not contain reflections from fcc or hcp fullerite C₇₀ phases. Comparison with data in [13] shows reflections from orthorhombic C₇₀ · C₆H₅CH₃ (A) ($a = 10.88 \text{ \AA}$, $b = 10.55 \text{ \AA}$, $c = 32.92 \text{ \AA}$) and monoclinic solvate (B) ($a = 10.63 \text{ \AA}$, $b = 10.58 \text{ \AA}$, $c = 33.47 \text{ \AA}$, $\beta = 94.9^\circ$). Presumably, the two DSC peaks (Fig. 1, curve 9) are due to the existence of two crystal solvates of various symmetries. The intensities of the lines of solvate B decrease noticeably upon heating to 109°C. After heating to 155°C, reflections characteristic of fullerite C₇₀ appear, along with the set of reflections from the orthorhombic solvate. Moderate intensities of lines and their small number make it impossible to decide in this case whether the fullerite structure is fcc or hcp. A further rise in temperature to 208°C makes the crystal solvate disappear, and the X-ray diffraction pattern corresponds to hcp fullerite C₇₀ (Fig. 3) with the unit cell parameters $a = 10.59 \text{ \AA}$, $c = 17.34 \text{ \AA}$. The aforesaid agrees with data in [19, 20]. Subsequent anneals at 200–400°C leave the structural state of the sample unchanged, as for the C₆₀-toluene system.

Let us consider the thermal stability and structural state of C₆₀-C₇₀-C₆H₅CH₃ ternary mixtures. Figure 1 illustrates DSC curves for samples with various C₇₀ proportions in C₆₀/C₇₀ mixtures. The table lists the temperatures of endothermic transformations and their enthalpies. Figure 4 illustrates the relevant X-ray diffraction patterns. The DSC curves change noticeably when C₇₀ substitutes for 1.9 wt % C₆₀. An endotherm is observed within 35–100°C. The peak associated with the degradation of the crystal solvate is nonsymmetrical (Fig. 1a). The enthalpy of transformation increases with increasing C₇₀ concentration to 4.8 wt %, while the peak asymmetry is conserved (Fig. 1b). A further rise in C₇₀ concentration increases the transformation temperature, i.e., increases the thermal stability of mixtures and decreases the enthalpy (table). When C₇₀ concentrations exceed 30 wt %, a second endotherm within

Onset temperatures (T_{on}) and end temperatures (T_{end}) and enthalpies (ΔH) of solvate decomposition for C₆₀-C₇₀-C₆H₅CH₃ samples with various C₇₀ weight percentages in C₆₀/C₇₀ mixtures

C ₇₀ , wt %	$T_{\text{on}} \pm 0.2, ^\circ\text{C}$	$T_{\text{end}} \pm 0.2, ^\circ\text{C}$	$\Delta H \pm 1.0, \text{ J/g}$
0	72.7	89.0	2.5
1.9	61.8	69.3	12.8
4.8	60.5	67.9	32.7
10	68.6	79.4	34.5
15	72.1	83.4	27.3
20	74.0	85.1	24.7
30	77.9	89.5	15.6
50	82.2	95.5	4.7
100	169.6	179.8	13.0
	144.3	155.9	7.3
	169.1	179.2	16.0

130–200°C becomes noticeable; in the 50 wt % C₇₀ sample, this second endotherm prevails over the first one. Importantly, the temperature of this second peak almost coincides with the crystal solvate degradation temperature in the C₇₀-C₆H₅CH₃ system [14].

Addition of C₇₀ to C₆₀-C₆H₅CH₃ samples does not change the set of lines characteristic of C₆₀ · C₆H₅CH₃, although the interplanar spacings and, as a result, the unit cell volume increase (Fig. 5). An additional set of lines positionally close to the C₇₀ · C₆H₅CH₃ lines but with smaller unit cell parameters becomes noticeable only in the mixture containing 50 wt % C₇₀. After heating to 100°C, the X-ray diffraction pattern retains the lines from a solvate with the composition close to orthorhombic C₇₀ · C₆H₅CH₃ but with a smaller unit cell volume. The intensities of the main lines from the C₆₀ and C₇₀ solvates are approximately equal, but the X-ray diffraction pattern of the 50 wt % C₆₀ + 50 wt % C₇₀ sample does not coincide with the patterns from the C₆₀ and C₇₀ solvates. In addition, the lines of fcc fullerite C₆₀ decrease in intensity with rising C₇₀ concentration and disappear in the 50 wt % C₇₀ sample. The fcc unit cell parameter is 14.187–14.208 Å, close to the parameter of the C₆₀-C₆H₅CH₃ system.

Presumably, fcc fullerites C₆₀ formed from solution at room temperature are almost free of fullerenes C₇₀. The increased unit cell parameter of C₆₀ relative to the reference ($a_{\text{ref}} = 14.166 \text{ \AA}$) is likely due to the occupation of octahedral pores in the fullerite lattices by gases and due to high structure imperfection [21, 22]. Its imperfection is proven by the absence of the peak from an orientational phase transition in the low-temperature part of DSC curves: this transition is very responsive to defect density [23]. After annealing in dynamic vacuum at 200–400°C, the fullerite unit cell parameters can remain increased despite the removal of molecular gases [24].

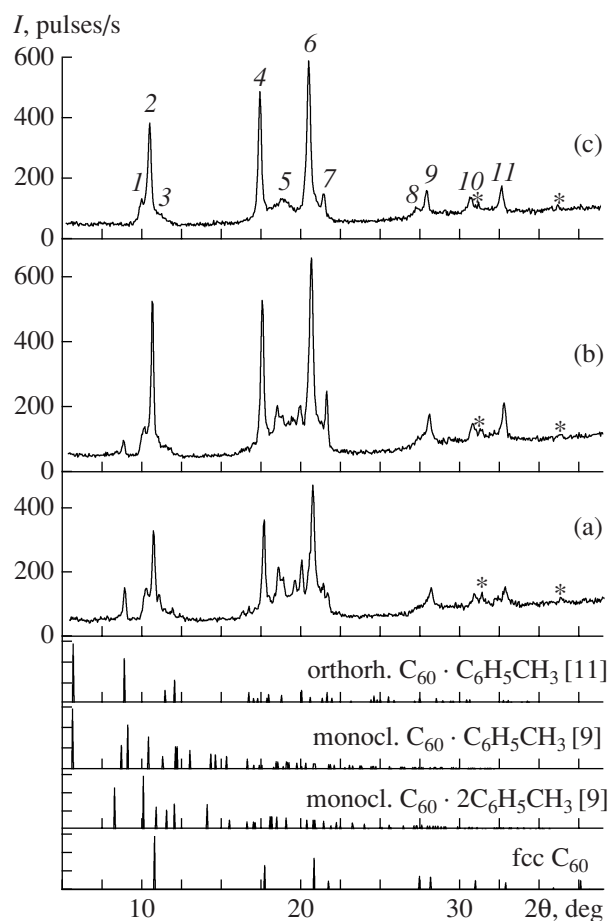


Fig. 2. X-ray diffraction patterns of (a) initially prepared C_{60} - $C_6H_5CH_3$ samples and (b, c) the same samples after heating to (b) 60 and (c) 109°C. In the lower part of the figure, X-ray diffraction diagrams for crystal solvate and fcc C_{60} phases; in the upper part, lines of fcc and hcp C_{60} phases are indicated: (1) hcp [100], (2) fcc [111]/hcp [002], (3) hcp [101], (4) fcc [220]/hcp [110], (5) hcp [103], (6) fcc [311]/hcp [112], (7) fcc [222]/hcp [004], (8) fcc [331]/hcp [121], (9) fcc [420]/hcp [114], (10) fcc [422], and (11) hcp [511]/hcp [333]. Lines from the cell material are marked with asterisks.

The isothermal treatment of all C_{60} - C_70 - $C_6H_5CH_3$ samples at 200°C for 2 h leads to the complete decomposition of crystal solvates (Fig. 6). Low- C_{70} samples are structurally similar to the samples obtained by annealing the C_{60} solvate. With rising C_{70} concentration, the intensity is reduced and the half-width of fcc- C_{60} lines increases, and the X-ray diffraction patterns resemble more the pattern of the hcp fullerite phase. However, separate lines of fullerite C_{70} are absent in all samples.

X-ray diffraction patterns for the 30 and 50 wt % C_{70} samples are of interest. For the 30 wt % C_{70} sample, the structure can be characterized by two phases: fcc fullerite C_{60} , which was found in all samples with lower C_{70} concentrations; and an hcp phase with the average unit

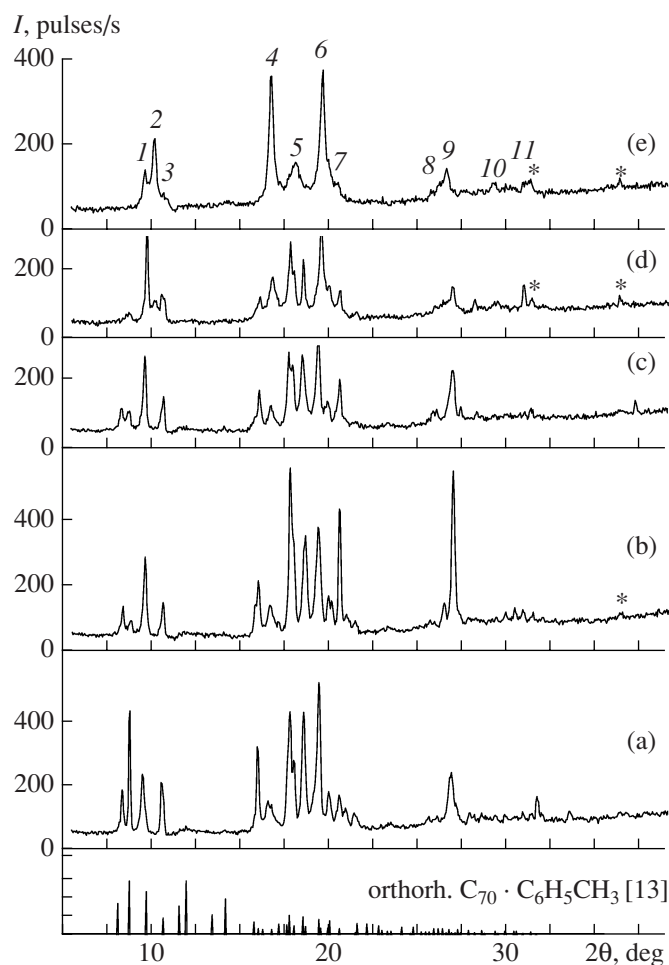


Fig. 3. X-ray diffraction patterns of (a) initially prepared C_{70} - $C_6H_5CH_3$ samples and (b-e) the same samples after heating to (b) 60, (c) 109, (d) 155, and (e) 208°C. In the lower part of the figure, the X-ray diffraction diagram for orthorhombic crystal solvate $C_{70} \cdot C_6H_5CH_3$; in the upper part, lines of hcp C_{70} are indicated: (1) [100], (2) [002], (3) [101], (4) [110], (5) [103], (6) [112], (7) [004], (8) [121], (9) [114], (10) [205], and (11) [006]. Lines from the cell material are marked with asterisks.

cell parameters $a = 10.15 \text{ \AA}$, $c = 16.70 \text{ \AA}$. (The reference values for hcp C_{60} are $a = 10.02 \text{ \AA}$, $c = 16.42 \text{ \AA}$ [25]; for C_{70} , $a = 10.60 \text{ \AA}$, $c = 17.30 \text{ \AA}$ [26]).

In the 50 wt % C_{70} sample, structural alteration is even greater. The set of lines shows the fcc and hcp major phases. The cubic phase has the average unit cell parameter $a \sim 14.24 \text{ \AA}$ (ranging from 14.197 to 14.368 $\text{\AA}$ for individual lines).¹ The broad low-intensity line near 19° can indicate the presence of an hcp phase based on fullerite C_{60} . The second phase has an hcp lattice with

¹ This determination of the unit cell parameter based on the last well recorded line, (113) in the case at hand, is incompletely adequate because of a considerable error and the possible existence of packing defects.

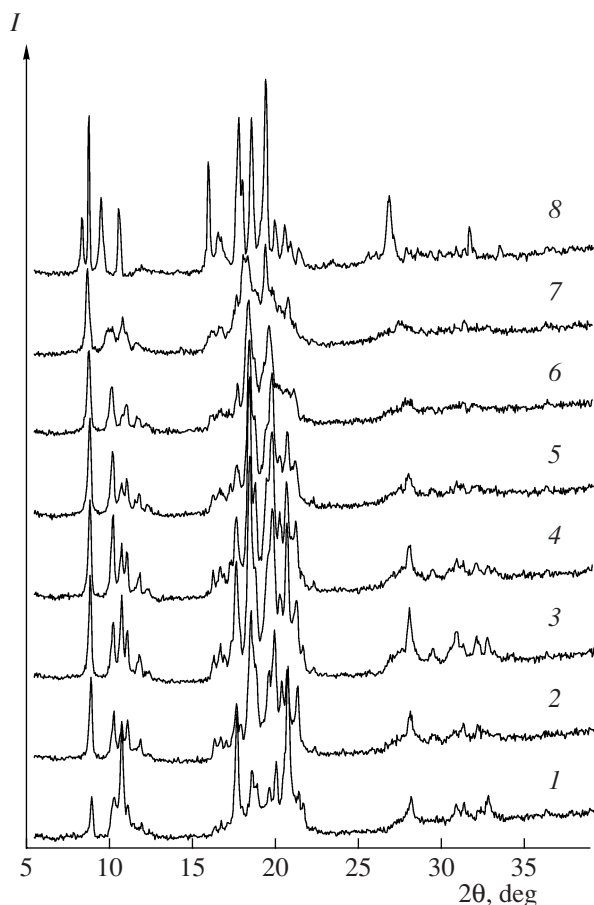


Fig. 4. X-ray diffraction patterns of initially prepared C₆₀-C₇₀-C₆H₅CH₃ samples containing (1) 0, (2) 4.8, (3) 10, (4) 15, (5) 20, (6) 30, (7) 50, and (8) 100 wt % C₇₀ in the C₆₀/C₇₀ mixture.

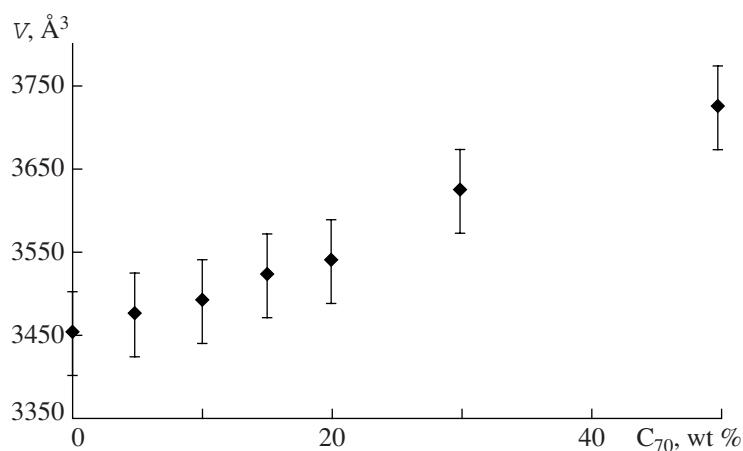


Fig. 5. Unit cell volume V of the crystal solvate (C₆₀, C₇₀) · C₆H₅CH₃ vs. C₇₀ concentration in the C₆₀/C₇₀ mixture.

average unit cell parameters $a \sim 10.45$ Å, $c \sim 17.16$ Å ($c/a = 1.64$). Assuming that the unit cell parameters are linear functions of concentration, the first phase is a substitutional solid solution based on fcc fullerite C₆₀

containing ~10 wt % C₇₀, whereas the second hcp phase is a C₇₀-based substitutional solid solution containing ~20–30 wt % C₆₀. Annealing at 400°C under the same conditions gives similar results.

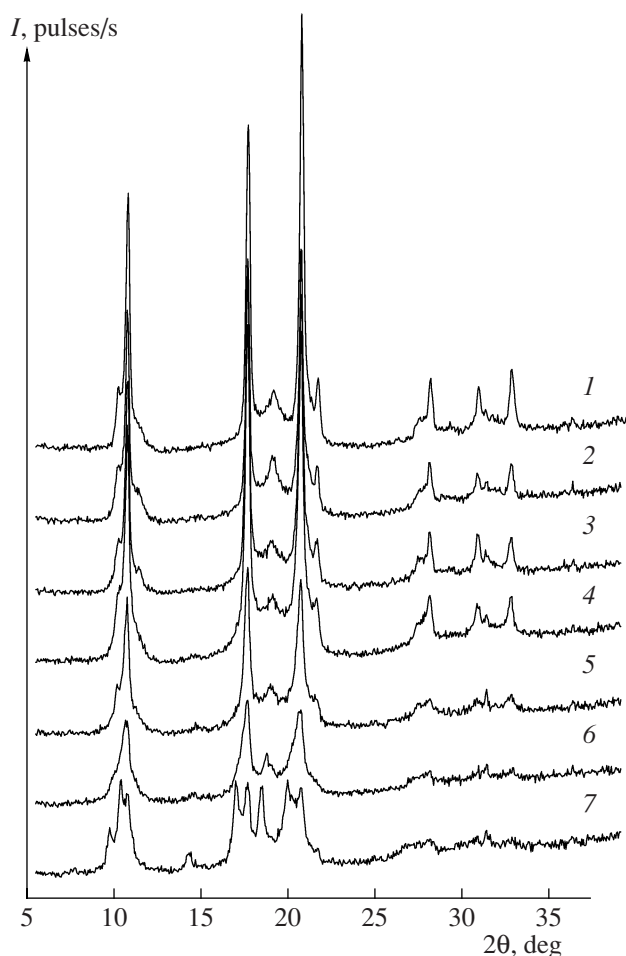


Fig. 6. X-ray diffraction patterns of C_{60} - C_{70} - $C_6H_5CH_3$ samples containing (1) 0, (2) 4.8, (3) 10, (4) 15, (5) 20, (6) 30, and (7) 50 wt % C_{70} in the C_{60}/C_{70} mixture after annealing at 200°C for 2 h.

To summarize, the results of our experimental studies show that the thermal stability of the C_{60} - C_{70} - $C_6H_5CH_3$ ternary crystal solvates and their lattice volumes increase with rising C_{70} concentration in the C_{60}/C_{70} mixture. In samples containing 50 wt % C_{70} , two types of crystal solvates are found to exist simultaneously, with structures close to $C_{60} \cdot C_6H_5CH_3$ and $C_{70} \cdot C_6H_5CH_3$ and temperature decomposition ranges of 80–96 and 160–180°C, respectively. The decomposition of C_{60} - C_{70} - $C_6H_5CH_3$ ternary crystal solvates of various compositions generates an hcp C_{60} - C_{70} solid solution.

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