

TERNARY SYSTEM OF C₆₀ AND C₇₀ WITH 1,2-DIMETHYLBENZENE

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ABSTRACT

Differential scanning calorimetry, X-ray, and solubility measurements were used to study phase equilibria in the ternary system C₆₀-C₇₀-1,2-dimethylbenzene up to the boiling point of the solvent. Formation of the two ternary phases was confirmed. Partial solubilities of C₆₀ and C₇₀ were measured and calculated.

INTRODUCTION

Extraction and fractional crystallization could play a certain role in the production of the pure fullerenes C₆₀ and C₇₀. To find the proper temperature and the proper solvent for dissolution of the fullerene mixtures is still a challenging goal. The conventional theoretical bases for the development of extraction and purification procedures are multicomponent phase diagrams, which supply information on equilibrium phase composition at different temperatures. To prepare

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such a diagram one needs to know Gibbs free energies of formation for all the solid/liquid phases in the system. Binary systems of C_{60} and C_{70} with different organic solvents have been extensively studied in recent years. The solubility of C_{60} at room temperature was measured in more than 100 solvents (1). Much less is known about the solubility of C_{70} (2,3). Partial solubilities of C_{60} and C_{70} in the ternary systems have never been examined.

It has been shown that both fullerenes alone form solid solvates with different solvents. The thermodynamics of these Van der Waals complexes was carefully studied in many cases (4–8). With 1,2-dimethylbenzene C_{60} forms the stoichiometric solvated crystal $C_{60} \cdot 2C_8H_{10}$. The enthalpy of decomposition of this crystal was found to be 31 ± 2 kJ/mol of C_{60} (8). In the binary system of C_{70} with 1,2-dimethylbenzene two incongruent melting points were observed with the decomposition enthalpies of 18.5 ± 1.5 and 23.0 ± 1.0 kJ/mol of C_{70} , respectively. The latter enthalpy corresponded to the decomposition of the solvated crystal composed of a $C_{70} \cdot 2C_8H_{10}$ formula unit while the former was attributed to the first step of decomposition of another solvated crystalline phase which incorporated at least one more molecule of 1,2-dimethylbenzene (8).

No binary solid compounds of C_{60} with C_{70} have been reported.

The only example of a ternary system studied was C_{60} and C_{70} with cyclohexane (9). X-ray analysis confirmed the formation of the solid solvate solutions $C_{60}/C_{70} \cdot 12C_6H_{12}$ in the whole concentration range with fcc elementary cell. It was shown that Vegard's law is valid for the ternary solvate given. Binary solvates $C_{70} \cdot 12C_6H_{12}$ and $C_{60} \cdot 12C_6H_{12}$ had isomorphous crystal structures (10).

In the present study an effort was made to examine ternary system of C_{60} and C_{70} with 1,2-dimethylbenzene. The problems at hand were formation of ternary solid phases, reaching of the true phase of equilibrium, and determination of partial solubilities of C_{60} and C_{70} .

EXPERIMENTAL

Samples of C_{60} were from Bucky USA and MER Ltd. (99.9% mol purity) and C_{70} was from MER Ltd. (99.5% mol purity). 1,2-Dimethylbenzene was a commercial sample of HP grade. The solvent was used without additional distillation.

Differential scanning calorimetry (DSC) was used to monitor the formation of solid solvates of fullerenes. DSC measurements were carried out with a Mettler DSC-30 instrument. Measurements were taken at temperatures from 190 up to 390 K. The scanning rates were usually 10 K/min. Maxima and onset temperatures were measured for all of the DSC peaks found. For the systems under study the latter temperatures were shown to be almost independent of scanning rate. The onset temperatures were considered to give the best estimation of the equilibrium phase transition temperatures.

Thirteen heterogeneous (solid different molar ratios of C_{60} to C_{70} and solvent to fullerenes were less than 10 than 98% of fullerenes were kept in the solution. The samples were prepared were prepared by mixing weighed an aluminum DSC pans and then sealing way of preparation included complete and C_{70} in 1,2-dimethylbenzene at room precipitated from the solution by evap at room temperature. For accelerating removed by the air flow in 2–3 h. The solid + liquid sample was then put into scanning (procedure B).

Each sample was scanned three samples were left to stand at room temper a period from 1/2 h up to 6 months. Data were compared to prove that the equilibrium the course of measurements. Further been described elsewhere (7,8).

DSC measurements showed the with the solvents. Formation of solvate peaks (10–25 kJ/mol of a fullerene, melting transitions and by disappearance fullerene), corresponding to solid-solid latter peaks reappeared again after the melting (down scan) (8). DSC measured the amount of solvent incorporated into analysis or thermogravimetry was unusual traces obtained with samples A and B. Some of the peaks were not detected preparation. We assumed that formation prevented by kinetic difficulties, which results presented in this paper were obtained.

Powder X-ray diffraction data were $CuK\alpha$. The samples were prepared according

Ternary and binary saturated liquid were prepared by stirring in a thermostat. The solution was stirred until it was level. The time specified was found to equilibrium. Solubilities of C_{60} and C_{70} spectrophotometrically using preliminary

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Thirteen heterogeneous (solid + saturated liquid solution) samples with different molar ratios of C₆₀ to C₇₀ and to the solvent were studied. Molar ratios of solvent to fullerenes were less than 10 in all of the samples. With such a ratio more than 98% of fullerenes were kept in the solid phase rather than in the saturated liquid solution. The samples were prepared in two different ways. Some of the samples were prepared by mixing weighed amounts of C₆₀, C₇₀, and the solvent within aluminum DSC pans and then sealing afterwards (procedure A). The alternative way of preparation included complete dissolution of the weighed amounts of C₆₀ and C₇₀ in 1,2-dimethylbenzene at room temperature. The solid phases were then precipitated from the solution by evaporation of most of the solvent for 1–3 days at room temperature. For accelerating the process, the excess solvent has been removed by the air flow in 2–3 h. The small part of the remaining heterogeneous solid + liquid sample was then put into the DSC pans. The pans were sealed prior to scanning (procedure B).

Each sample was scanned three to six times. Before each measurement sam- ples were left to stand at room temperature or at $T = 260$ K in the refrigerator for a period from 1/2 h up to 6 months. Data for the samples with a different prehistory were compared to prove that the equilibrium phase composition was reached in the course of measurements. Further details of the experimental procedure have been described elsewhere (7,8).

DSC measurements showed the formation of solid solvates of C₆₀ and C₇₀ with the solvents. Formation of solvates was proved by the appearance of new peaks (10–25 kJ/mol of a fullerene, up scan), corresponding to the incongruent melting transitions and by disappearance of the smaller peaks (5–8 kJ/mol of a fullerene), corresponding to solid-solid phase transitions in pure fullerenes. These latter peaks reappeared again after the solid solvate was destroyed by incongruent melting (down scan) (8). DSC measurements were also employed to determine the amount of solvent incorporated into the solvates, since conventional chemical analysis or thermogravimetry was unsuitable for the samples under study. The DSC traces obtained with samples A and B of the same composition were not identical. Some of the peaks were not detected with samples A even several months after preparation. We assumed that formation of some of the equilibrium phases was prevented by kinetic difficulties, which were more pronounced in case A. The final results presented in this paper were obtained with the samples B.

Powder X-ray diffraction data were taken with the DRON-3 instrument, CuK α . The samples were prepared according to procedure B.

Ternary and binary saturated liquid solutions for solubility measurements were prepared by stirring in a thermostatic cell ($T = 298 \pm 0.5$ K) for 6–24 h. The solution was stirred until it was found that solubility reached a constant level. The time specified was found to be adequate for establishing the solubility equilibrium. Solubilities of C₆₀ and C₇₀ in 1,2-dimethylbenzene were measured spectrophotometrically using preliminary calibration and the simple method of

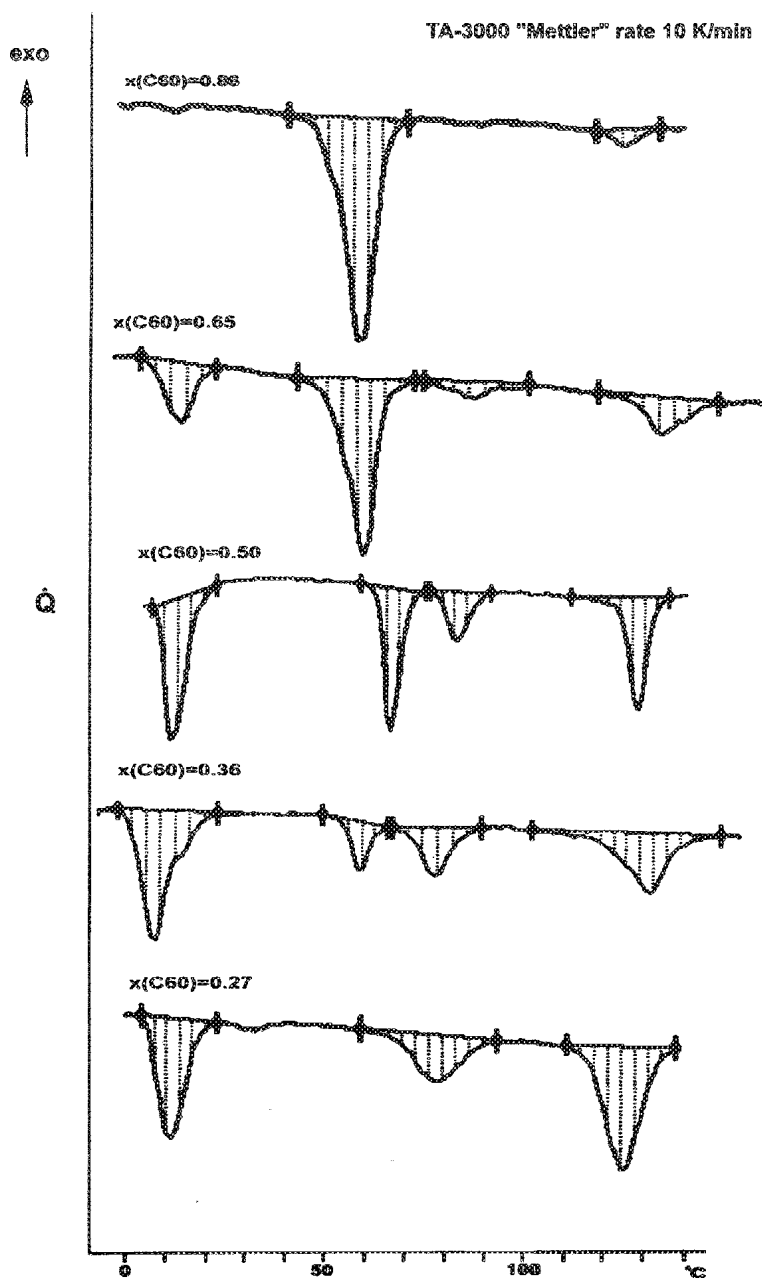


Figure 1. Typical DSC traces of the ternary system C_{60} - C_{70} -1,2-dimethylbenzene $x(C_{60})$ -fullerene molar fraction $\nu(C_{60})/(\nu(C_{60}) + \nu(C_{70}))$ in the sample.

C_{60} - C_{70} -1,2-DIMETHYLBENZENE

two waves in the case of ternary 1:1:1.62. The molar extinction coefficient $\epsilon(C_{70}) = 29,968 \pm 649 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon(C_{60}) = 424 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon(C_{60}) \approx 0$ were measured using a SPECORD ultraviolet-visible instrument. The molar extinction coefficients of the fullerenes in the concentration range 10^{-5} to 10^{-6} M for C_{70} . Molar extinction coefficients standard deviations shown above. The molar extinction coefficient of C_{60} to C_{70} was additionally checked.

RESULTS

Formation of the

Ternary solid samples with different compositions (1:1:1.62) were examined. Typical DSC traces are shown in Figure 1.

The data on the peaks observed in the DSC traces are presented in Table 1 along with the molar fractions of 1,2-dimethylbenzene and C_{70} -1,2-dimethylbenzene.

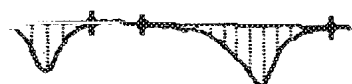
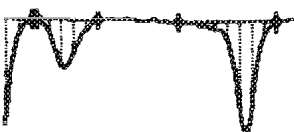
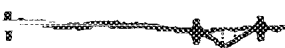
Table 1. DSC Peaks in the Ternary System C_{60} - C_{70} -1,2-Dimethylbenzene

Temperature of the peak (onset), K	Temperature of the peak (maximum), K	Composition
323 ± 3	329 ± 3	$(C_{60})_1(C_{70})_1(1,2\text{-DMB})_1$
		$(C_{60})_1(C_{70})_1(1,2\text{-DMB})_1$
		$(C_{60})_1(C_{70})_1(1,2\text{-DMB})_1$
274 ± 3	283 ± 3	$(C_{60})_1(C_{70})_1(1,2\text{-DMB})_{1.5}$
344 ± 6	350 ± 6	$(C_{60})_1(C_{70})_1(1,2\text{-DMB})_{1.5}$
391 ± 3	396 ± 3	$(C_{60})_1(C_{70})_1(1,2\text{-DMB})_{1.5}$
310 ± 1	320 ± 2	$C_{60}S_2(C_{70})_1$
365 ± 1	368.7 ± 0.8	$C_{70}S_2(C_{60})_1$

^a See text for more discussion.

^b Data from Ref. 8.

TA-3000 "Mettler" rate 10 K/min



system C₆₀-C₇₀-1,2-dimethylbenzene $x(C_{60})$ -
 $(1-x)(C_{70})$ in the sample.

two waves in the case of ternary liquid solutions. Analytical wavelengths $\lambda_1 = 333.6$ nm [molar extinction coefficient values $\epsilon(C_{60}) = 44,712 \pm 542 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon(C_{70}) = 29,968 \pm 649 \text{ M}^{-1} \text{ cm}^{-1}$] and $\lambda_2 = 485.6$ nm [$\epsilon(C_{70}) = 17,630 \pm 424 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon(C_{60}) \approx 0$] were used. Measurements were taken with the SPECORD ultraviolet-visible instrument. Calibration curves were prepared for fullerenes in the concentration ranges $(0.74\text{--}5.17) \cdot 10^{-5}$ M for C₆₀ and $(1.65\text{--}8.21) \cdot 10^{-5}$ M for C₇₀. Molar extinction coefficients were constant within the standard deviations shown above. The reliability of the measured ratio of solubilities C₆₀ to C₇₀ was additionally checked by high-performance liquid chromatography.

RESULTS AND DISCUSSION

Formation of the Ternary Solid Solvates

Ternary solid samples with different molar ratios of C₆₀ to C₇₀ from 11.3:1 up to 1:16.2 were examined. Typical DSC curves of certain samples B are presented in Figure 1.

The data on the peaks observed in the system C₆₀-C₇₀-1,2-dimethylbenzene are presented in Table 1 along with the literature data on the binary systems C₆₀-1,2-dimethylbenzene and C₇₀-1,2-dimethylbenzene (8). As is seen from Table 1, peaks

Table 1. DSC Peaks in the Ternary System C₆₀-C₇₀-1,2-Dimethylbenzene and in the Binary Systems C₆₀-1,2-Dimethylbenzene and C₇₀-1,2-Dimethylbenzene

Temperature of the peak (onset), K	Temperature of the peak (maximum), K	The Process Assumed ^a
323 ± 3	329 ± 3	$(C_{60})_x(C_{70})_{1-x}S_n(s, I) = xC_{60}(s) + (1-x)C_{70}(s) + nS(\text{liq})$ $(C_{60})_x(C_{70})_{1-x}S_n(s, I) = \{1 - \frac{1-x'}{1-x''}\}C_{60}(s) + \frac{1-x'}{1-x''}(C_{60})_x''(C_{70})_{1-x''}S_m(s, II) + \{n - m\frac{1-x'}{1-x''}\}S(\text{liq})$
274 ± 3	283 ± 3	$(C_{60})_x''(C_{70})_{1-x''}S_{m+1}(s) = (C_{60})_x''(C_{70})_{1-x''}S_m(s, II) + 1S(\text{liq})$
344 ± 6	350 ± 6	$(C_{60})_x''(C_{70})_{1-x''}S_m(s, II) = (C_{60})_x''(C_{70})_{1-x''}S_k(s, II') + (m-k)S(\text{liq})$
391 ± 3	396 ± 3	$(C_{60})_x''(C_{70})_{1-x''}S_k(s, II') = x''(C_{60})(s) + (1-x'')C_{70}(s) + kS(\text{liq})$
310 ± 1	320 ± 2	$C_{60}S_2(s) = C_{60}(s) + 2S(\text{liq})^b$
365 ± 1	368.7 ± 0.8	$C_{70}S_2(s) = C_{70}(s) + 2S(\text{liq})^b$

^a See text for more discussion.

^b Data from Ref. 8.

found in the ternary system are different from peaks observed earlier in the binary systems C_{60} -1,2 dimethylbenzene and C_{70} -1,2 dimethylbenzene.

Peak at $T = 391 \pm 3$ K

The temperature of this effect was well above those for the effects observed in the binary systems. The peak was seen with the samples of all the compositions studied. The enthalpy of the peak per mole of C_{70} depended on the initial composition of the sample and reached its maximum at the $C_{60}:C_{70}$ molar ratio close to 1:3. With the samples containing more C_{70} the peak at 365 K (onset) was observed, which corresponded to decomposition of the binary solvate $C_{70} \cdot 2C_8H_{10}$ ($C_{70}S_2$). Comparison of the data obtained from both sides of the 1:3 composition proved the formation of the ternary solid solvate. The peak at 391 ± 3 K was easily detected with both samples A and B.

Peak at $T = 344 \pm 6$ K

The enthalpy of this endotherm depended on the $C_{60}:C_{70}$ molar ratio in the same manner as the enthalpy of the endotherm at $T = 391 \pm 3$ K. Thus, a two-step decomposition of the ternary solvate with the molar ratio of $C_{60}:C_{70}$ around 1:3 was suggested. It should be mentioned that both the temperature and the enthalpy of the effect at $T = 344 \pm 6$ K were less reproducible, compared to the effect at 391 ± 3 K. The former peak was broad and sometimes of irregular shape, especially with the samples A.

Peak at $T = 323 \pm 3$ K

The enthalpy of this endotherm for the samples rich in C_{60} was practically equal to the enthalpy of decomposition of the binary solvate $C_{60} \cdot 2C_8H_{10}$ ($C_{60}S_2$), while the temperature was 10° higher than that of the corresponding binary solvate. This peak was rarely detected with the samples A.

X-Ray Diffraction

Room temperature X-ray powder diffraction patterns of the ternary samples with different molar ratios of C_{60} to C_{70} are presented in Figure 2. X-ray data confirmed the formation of the ternary phases. It could be supposed that the samples

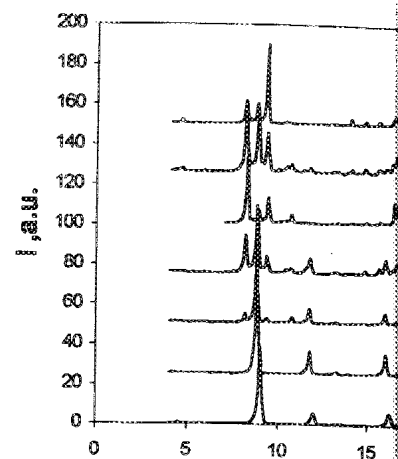


Figure 2. X-ray powder diffraction patterns.

rich with C_{60} [e.g., $x(C_{60}) = 0.86^*$ in the structure of the binary solvate $C_{60}S_2$] in X-ray diffraction it was not possible to carefully determine which phase I was stable, though it was supposed that $x(C_{60}) = 0.86$ was phase I. Parameters of the phases are presented in Table 2. The appearance of a peak at 323 ± 3 K with increasing C_{70} content in the solid phase [$x(C_{60})$ decreasing] suggested the formation of another ternary phase with a crystal structure similar to that of the binary solvates [$x(C_{60}) = 1$ and $x(C_{70}) = 1$ in the binary systems].

Determination of the Composition of the Phases

Based on the DSC and X-ray data the composition of the solid solvates was suggested. They are:

Phase I, a solid solution with a crystal structure similar to that of the binary solvate, which has an endotherm at $T = 323 \pm 3$ K corresponding to the formation of a certain quantity of the solid solvate (it is clear that the mole fraction of C_{60} in the liquid solution [reaction (1)] or with the solid and liquid solution (practically pure solid solvate).

*Here and below $x(C_{60})$, fullerene molar fraction in the liquid solution $\nu(C_{60})/\nu(C_{60}) + \nu(C_{70})$.

from peaks observed earlier in the binary C_{70} -1,2 dimethylbenzene.

$T = 391 \pm 3$ K

well above those for the effects observed with the samples of all the compositions. The peak of C_{70} depended on the initial composition. The maximum at the C_{60} : C_{70} molar ratio close to 1:3 the peak at 365 K (onset) was observed, and the binary solvate $C_{70} \cdot 2C_8H_{10}$ ($C_{70}S_2$). On both sides of the 1:3 composition proved the peak at 391 ± 3 K was easily detected

$T = 344 \pm 6$ K

depended on the C_{60} : C_{70} molar ratio in the therm at $T = 391 \pm 3$ K. Thus, a two-step with the molar ratio of C_{60} : C_{70} around 1:3 that both the temperature and the enthalpy is reproducible, compared to the effect at and sometimes of irregular shape, especially

$T = 323 \pm 3$ K

for the samples rich in C_{60} was practically of the binary solvate $C_{60} \cdot 2C_8H_{10}$ ($C_{60}S_2$), in that of the corresponding binary solvate. samples A.

Diffraction

Diffraction patterns of the ternary samples are presented in Figure 2. X-ray data are given in Table 1. It could be supposed that the samples

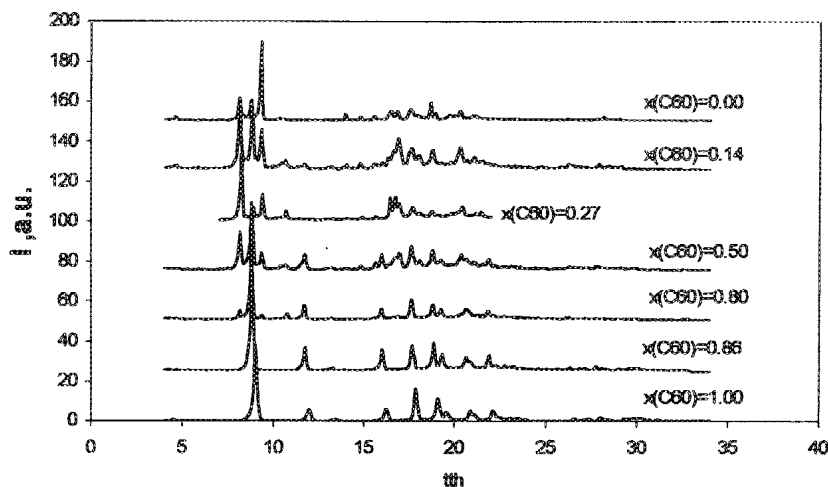


Figure 2. X-ray powder diffraction patterns of the ternary system.

rich with C_{60} [e.g., $x(C_{60}) = 0.86^*$ in Figure 2] were solid solutions based on the structure of the binary solvate $C_{60}S_2$ [$x(C_{60}) = 1$ in Figure 2] (phase I). With X-ray diffraction it was not possible to carefully determine the concentration range in which phase I was stable, though it was believed that most of the solid phase at $x(C_{60}) = 0.86$ was phase I. Parameters of the cell for the phase I [$x(C_{60}) = 0.86$] are presented in Table 2. The appearance of new reflections with increasing of the C_{70} content in the solid phase [$x(C_{60}) \leq 0.80$ in Figure 2] testified to the presence of another ternary phase with a crystal structure different from those of the binary solvates [$x(C_{60}) = 1$ and $x(C_{70}) = 1$ in Figure 2].

Determination of the Composition of the Ternary Solvates

Based on the DSC and X-ray data described above, formation of two ternary solid solvates was suggested. They are:

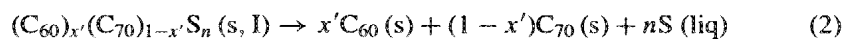
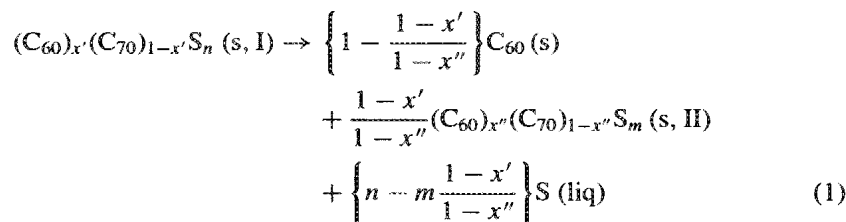
Phase I, a solid solution with a crystal lattice similar to that of $C_{60}S_2$. The endotherm at $T = 323 \pm 3$ K corresponds to decomposition of this phase with formation of a certain quantity of the more stable phase II and unsolvated C_{60} (it is clear that the mole fraction of C_{60} in phase I exceeds that in phase II) and liquid solution [reaction (1)] or with the formation of pure unsolvated fullerenes and liquid solution (practically pure solvent) [reaction (2)]. Reaction (1) is an

*Here and below $x(C_{60})$, fullerene molar fraction in the ternary system, is equal to $v(C_{60})/v(C_{60}) + v(C_{70})$.

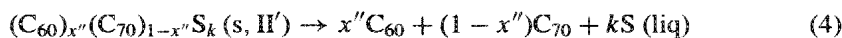
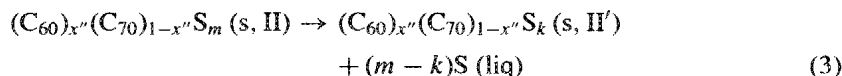
Table 2. The Parameters of the Elementary Cell of the Binary Solvate and Phase I

	a	b	C	α	β	γ	V	Z
C ₆₀ S ₂	15,33 (1)	13,08 (4)	10,01 (3)	90	99,4 (1)	90	1980	2
Phase I	15,46 (1)	13,20 (2)	10,21 (1)	90	99,87 (8)	90	2053	2

equilibrium process. It was decided however that under the conditions of our DSC experiment the reaction (2) took place (see below).



Phase II, with the molar ratio of C₆₀ to C₇₀ close to 1:3. Endotherms at $T = 344 \pm 6$ K and $T = 391 \pm 3$ K corresponded to the two-step loss of solvent from this phase [reactions (3) and (4)]. The molar ratio of C₆₀ to C₇₀ in phase II below and above 344 K was considered to be the same. The endotherm near 274 ± 3 K (see Table 1) proved that phase II could hold even more solvent molecules. The enthalpy of this process changed in proportion with enthalpies measured at 391 K and 344 K, while composition of the samples was changed (see Fig. 1).



Samples with the molar ratio of C₆₀ and C₇₀ from 11:1 up to 1:2.5 were considered to be heterogeneous mixtures of phases I and II below 323 K.

Simple mass balance equations correlated measured enthalpies $\Delta H(323 \text{ K})$, $\Delta H(344 \text{ K})$, and $\Delta H(391 \text{ K})$ of the processes at $T = 323 \pm 3$ K, $T = 344 \pm 6$ K, $T = 391 \pm 3$ K to the fullerene molar fraction of C₆₀ in the sample, $x(C_{60}) = v(C_{60}) / \{v(C_{60}) + v(C_{70})\}$. For $\Delta H(323 \text{ K})$ one gets:

$$\begin{aligned}
 \Delta H(323 \text{ K}) / \{v(C_{60}) + v(C_{70})\} \\
 = \Delta H^0(323 \text{ K}) \cdot [x(C_{60}) - x''(C_{60})] / \{x'(C_{60}) - x''(C_{60})\} \quad (5)
 \end{aligned}$$

where $\Delta H^0(323 \text{ K})$ is the enthalpy of reaction (1) or (2), $x'(C_{60})$ and $x''(C_{60})$ are fullerene molar fractions of C₆₀ in phases I and II, respectively. The least-square treatment of the dependence $\Delta H(323 \text{ K}) / \{v(C_{60}) + v(C_{70})\}$ vs. $x(C_{60})$ for

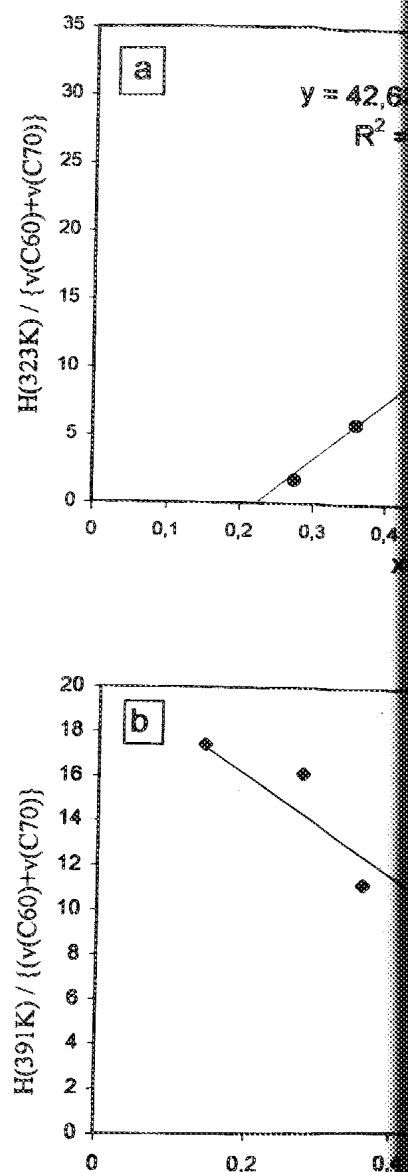


Figure 3. a. Dependence of the enthalpy versus fullerene molar fraction of C₆₀ in the effect at 391 K per mole of fullerenes versus

Cell of the Binary Solvate and Phase I

	α	β	γ	V	Z
i)	90	99,4 (1)	90	1980	2
ii)	90	99,87 (8)	90	2053	2

er that under the conditions of our DSC
e below).

$$\left. \begin{array}{l} -x' \\ -x'' \end{array} \right\} C_{60} (s)$$

$$\left. \begin{array}{l} x' \\ x'' \end{array} \right\} (C_{60})_{x'}(C_{70})_{1-x''}S_m (s, II)$$

$$\left. \begin{array}{l} 1-x' \\ 1-x'' \end{array} \right\} S (liq) \quad (1)$$

$$) + (1-x')C_{70} (s) + nS (liq) \quad (2)$$

, to C₇₀ close to 1:3. Endotherms at $T =$
ded to the two-step loss of solvent from
lar ratio of C₆₀ to C₇₀ in phase II below
e same. The endotherm near 274 ± 3 K
hold even more solvent molecules. The
rtion with enthalpies measured at 391 K
ples was changed (see Fig. 1).

$$r''(C_{70})_{1-x''}S_k (s, II')$$

$$-k)S (liq) \quad (3)$$

$$) + (1-x'')C_{70} + kS (liq) \quad (4)$$

70 from 11:1 up to 1:2.5 were considered
and II below 323 K.

elated measured enthalpies ΔH (323 K),
esses at $T = 323 \pm 3$ K, $T = 344 \pm 6$ K,
tion of C₆₀ in the sample, $x(C_{60}) = v(C_{60})/$
gets:

$$C_{60})]/\{x'(C_{60}) - x''(C_{60})\} \quad (5)$$

reaction (1) or (2), $x'(C_{60})$ and $x''(C_{60})$
phases I and II, respectively. The least-
323 K)/ $\{v(C_{60}) + v(C_{70})\}$ vs. $x(C_{60})$ for

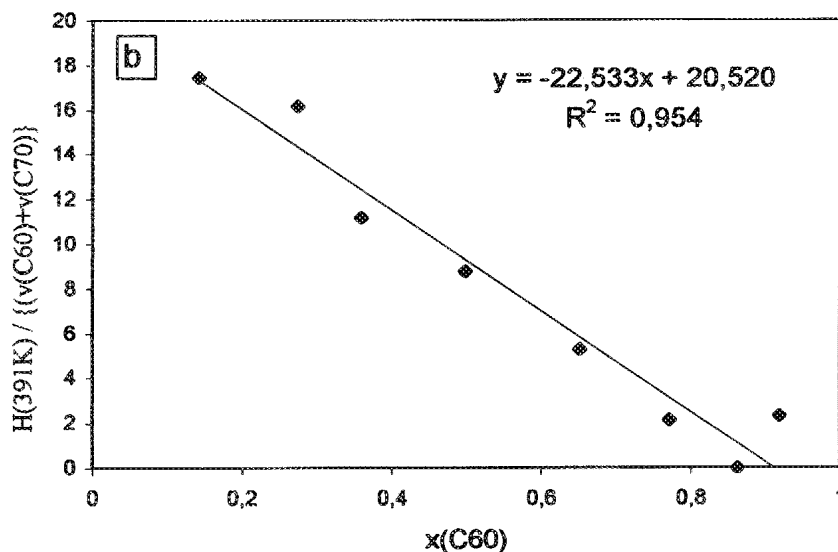
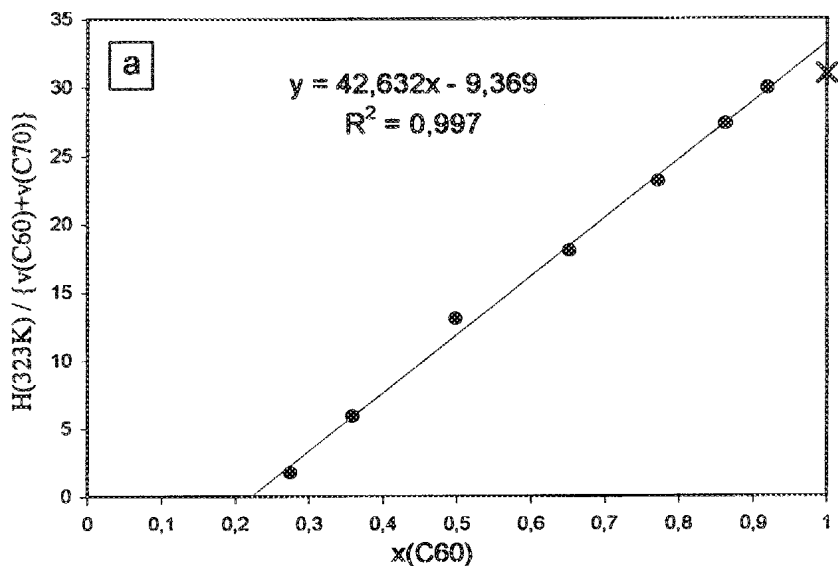


Figure 3. a. Dependence of the enthalpy of the effect at 323 K per mole of fullerenes versus fullerene molar fraction of C₆₀ in the sample. b. Dependence of the enthalpy of the effect at 391 K per mole of fullerenes versus fullerene molar fraction of C₆₀ in the sample.

the seven compositions studied is presented in Figure 3a. The ratio

$$-a/b = 9.37/42.63 = x''(C_{60}) = 0.22$$

in Figure 3a give the molar fraction of C_{60} in phase II. Reaction (2) rather than reaction (1) was taken as the decomposition process for phase I, since a slight dependence of the enthalpy $\Delta H(391 \text{ K})/\{v(C_{70})\}$ on $x(C_{60})$ was observed. With the samples rich with C_{60} this value was lower. It means that C_{70} from phase I did not go into the phase II after decomposition. It should be emphasized that the value of $x''(C_{60})$ did not depend on what decomposition reaction was chosen.

A similar treatment of the dependence $\Delta H(391 \text{ K})/\{v(C_{60}) + v(C_{70})\}$ vs. $x(C_{60})$ (Fig. 3b) was used to calculate the composition of phase I. The average value of $x'(C_{60}) = 0.92$ was obtained. According to DSC data, phase I existed in the concentration range $0.92 \leq x(C_{60}) \leq 1$.

With the knowledge of $x'(C_{60})$ and $x''(C_{60})$ one easily gets $\Delta H^0(323 \text{ K})$, $\Delta H^0(344 \text{ K})$, and $\Delta H^0(391 \text{ K})$ which correspond to phase reactions (2), (3), and (4).

The amount of solvent incorporated into the ternary solvates, was determined using the method described in Ref. 5. In the same runs, the DSC peak corresponding to the melting enthalpy of the solvent ($T = 248 \text{ K}$) was measured, after the fullerenes were completely converted into solvates. In this way the amount of extra solvent that had melted and thus had not reacted with fullerenes was determined. With prior knowledge of the total amount of fullerene and solvent in the samples, the molar ratios of C_8H_{10} to $\{C_{60} + C_{70}\}$ in the solvates were estimated. Measurements with the samples rich with C_{60} gave the complete composition of phase I as 2 mol of 1,2-dimethylbenzene per mol of fullerenes which coincided with the composition of the binary solvate of C_{60} . The amount of solvent in phase II was 4 mol per 1 mol of $\{0.22C_{60} + 0.78C_{70}\}$ below 274 K. At this temperature the first incongruent melting took place. The amount of solvent in phase II above room temperature and above $T = 344 \text{ K}$ could be estimated only roughly. The compositions of phases I and II along with the enthalpies and temperatures of the decomposition reactions (2) and (3,4) are presented in Table 3.

Table 3. Thermochemical Properties and Compositions of the Ternary Phases

Phase	T, K	ΔH (2),		ΔH (3),		ΔH (4),		$x(C_{60})^a$
		kJ/mol	T_1 , K	kJ/mol	T_2 , K	kJ/mol		
I	323 ± 3	31 ± 2	— ^b	—	—	—	—	$x' = 0.92 \pm 0.03$
II	—	—	344 ± 6	8.6 ± 1.0	391 ± 3	16.8 ± 1.0	—	$x'' = 0.22 \pm 0.01$

^a $x(C_{60})$ —fullerene mole fraction of C_{60} in the ternary phases.

^b Phase I: $(C_{60})_{0.92}(C_{70})_{0.08}S_2$; phase II: $(C_{60})_{0.22}(C_{70})_{0.78}S_m$, where $m = 4$ at $T \leq 280 \text{ K}$, $m \approx 2$ at $274 \text{ K} < T < 344 \text{ K}$.

Table 4. Thermodynamics of For

Reaction
$0.92 C_{60}S_2 + 0.08 C_{70}S_2 = \text{phase I (6)}$
$0.22 C_{60}S_2 + 0.78 C_{70}S_2 = \text{phase II (7)}$

Thermodyna

In Table 4 the enthalpies and the $C_{60}S_2$ and $C_{70}S_2$ to form phases I and II. The data were taken from the literature data for the binary solvates. The enthalpies of ideal mixing of the binary solvates. The entropies of mixing were calculated using the formula $\Delta_r H/T_{inc.m}$. Both $\Delta_r S$ and $\Delta_r H$ were within the temperature range from 298 to 344 K. The enthalpies of mixing are slightly negative, while the mixing values.

Phase I can be considered as a solid solution of $C_{60}S_2$. X-ray data for phase I resemble the cell in phase I is larger, since the C_{60} is larger (see Table 2). The Gibbs free energy of phase I is lower than that of phase II.

X-ray diffraction patterns for phases I and II. The Gibbs free energy of phase I is lower than that of phase II. The Gibbs free energy of the ideal mixing of $C_{60}S_2$ and $C_{70}S_2$ is -1.7 and -1.3 kJ/mol, respectively.

It is interesting to note that the enthalpy of mixing was similar to the same gap found in the binary system at molar ratio of $C_{60}/C_{70} = 0.22$ in phase II. Phase II possibly could be considered as a solid solution of C_{60} and C_{70} with the other systems of C_{60} and C_{70} with the other solvents. The C_{60} - C_{70} -1,2-dichlorobenzene system.

Ternary Phase D

C₆₀-C₇₀-1,2-

The sketch of the phase diagram is presented in Figure 4. The upper part of the diagram shows the phase diagram of the C_{60} - C_{70} -1,2-dimethylbenzene system.

ted in Figure 3a. The ratio

0.22

C₆₀ in phase II. Reaction (2) rather than
 tion process for phase I, since a slight
 /{v(C₇₀)} on x(C₆₀) was observed. With
 is lower. It means that C₇₀ from phase I
 s position. It should be emphasized that the
 decomposition reaction was chosen.

ence $\Delta H(391 \text{ K})/\{v(\text{C}_{60}) + v(\text{C}_{70})\}$ vs.
 he composition of phase I. The average
 according to DSC data, phase I existed in
 ≤ 1 .

d $x''(\text{C}_{60})$ one easily gets $\Delta H^0(323 \text{ K})$,
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into the ternary solvates, was determined
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 nt ($T = 248 \text{ K}$) was measured, after the
 o solvates. In this way the amount of extra
 t reacted with fullerenes was determined.
 t of fullerene and solvent in the samples,
 in the solvates were estimated. Measure-
 ave the complete composition of phase I
 ol of fullerenes which coincided with the
 o. The amount of solvent in phase II was
 o) below 274 K. At this temperature the
 he amount of solvent in phase II above
 K could be estimated only roughly. The
 ith the enthalpies and temperatures of the
 e presented in Table 3.

and Compositions of the Ternary Phases

3), ol	$T_2, \text{ K}$	$\Delta H(4),$ kJ/mol	$x(\text{C}_{60})^a$
—	—	—	$x' = 0.92 \pm 0.03$
1.0	391 ± 3	16.8 ± 1.0	$x'' = 0.22 \pm 0.01$

he ternary phases.

$(\text{C}_{60})_{0.22}(\text{C}_{70})_{0.78}\text{S}_m$, where $m = 4$ at $T \leq$

Table 4. Thermodynamics of Formation of Phases I and II ($T = 298\text{--}391 \text{ K}$)

Reaction	$\Delta H,$ kJ/mol	$\Delta S,$ J/mol · K	$\Delta S, \text{ J/mol} \cdot \text{ K}$ Ideal Mixing
$0.92 \text{ C}_{60}\text{S}_2 + 0.08 \text{ C}_{70}\text{S}_2 = \text{phase I (6)}$	-0.7	1.1	2.1
$0.22 \text{ C}_{60}\text{S}_2 + 0.78 \text{ C}_{70}\text{S}_2 = \text{phase II (7)}$	-0.6	3.6	4.4

Thermodynamic Consideration

In Table 4 the enthalpies and the entropies of mixing of the binary solvates C₆₀S₂ and C₇₀S₂ to form phases I and II, calculated from the data in Table 3 and from the literature data for the binary solvates, are compared with those for the ideal mixing of the binary solvates. Entropies of Equations (2)–(4) necessary to calculate the entropies of mixing were obtained as for the phase reactions, $\Delta_r S = \Delta_r H/T_{\text{inc.m}}$. Both $\Delta_r S$ and $\Delta_r H$ were considered to be temperature independent within the temperature range from 298 to 391 K. As is seen from the Table 4, the enthalpies of mixing are slightly negative, while the entropies are close to the ideal mixing values.

Phase I can be considered as a solid solution, based on the crystal structure of C₆₀S₂. X-ray data for phase I resembled those for the binary phase. The volume of the cell in phase I is larger, since the C₇₀ unit is larger, compared to the C₆₀ sphere (see Table 2). The Gibbs free energy of reaction (6) is -1.3 kJ/mol at $T = 310 \text{ K}$.

X-ray diffraction patterns for phase II are different from those of C₇₀S₂ or C₆₀S₂ phases. The Gibbs free energy of reaction (7) in Table 4 slightly exceeds the Gibbs free energy of the ideal mixing of the binary solvated phases, $0.22 \text{ C}_{60}\text{S}_2$ and $0.78 \text{ C}_{70}\text{S}_2$ (-1.7 and -1.3 kJ/mol , respectively, at $T = 310 \text{ K}$).

It is interesting to note that the miscibility gap found in the ternary system was similar to the same gap found in the unsolvated binary system C₆₀-C₇₀. The molar ratio of C₆₀/C₇₀ = 0.22 in phase II was practically equal to the same ratio at the miscibility gap border from the C₇₀-rich side in the C₆₀-C₇₀ system (11, 12). Phase II possibly could be considered as a solvated solid solution of C₆₀ and C₇₀. If that is true, "phase II" with the same C₆₀/C₇₀ ratio could be found in the ternary systems of C₆₀ and C₇₀ with the other solvents. We found such a similar phase in the C₆₀-C₇₀-1,2-dichlorobenzene system.

Ternary Phase Diagram for the System C₆₀-C₇₀-1,2-Dimethylbenzene

The sketch of the phase diagram of the system ($P = 1 \text{ atm}$, $T = 298 \text{ K}$) is presented in Figure 4. The upper part of the diagram (above the line of binary

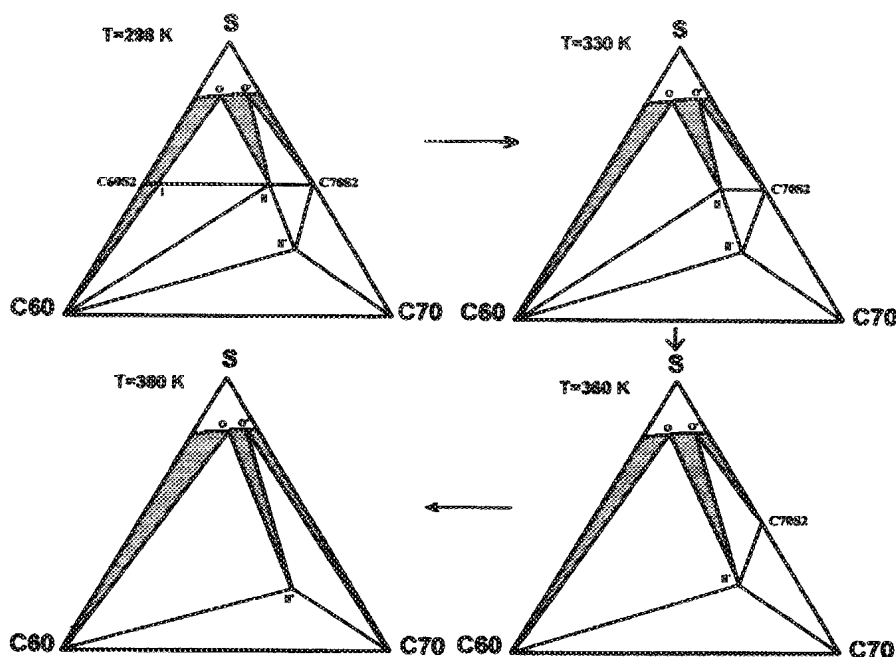


Figure 4. Isothermic cross-sections of the phase diagram of the system C_{60} - C_{70} -1,2-dimethylbenzene.

solvates $C_{60}S_2$ - $C_{70}S_2$) represents the equilibria with the saturated liquid solutions. This upper part includes two three-phase regions (phase I-phase II-saturated liquid solution O) and (phase II- $C_{70}S_2$ -saturated liquid solution O'), along with the three two-phase regions (phase I, phase II, and $C_{70}S_2$ with their saturated liquid solutions, respectively). Figure 4 represents the evolution of the diagram with the temperature at $P = 1$ atm. After successive decomposition of solvates at $T = 323$, 344, 365, and 391 K, unsolvated fullerenes C_{60} and C_{70} are in equilibrium with the saturated liquid solution above $T = 391$ K. The sketches in Figure 4 are based on the Gibbs free energies of formation of the phases I and II from binary solvates [ΔG (6) and ΔG (7), respectively], calculated from the data in Tables 3 and 4. Enthalpies and entropies of reactions (2) and (3, 4) were considered to be temperature-independent. Possible formation of solid solutions of the pure, unsolvated fullerenes were neglected.

The compositions of the saturated liquid solutions (Table 5) were estimated under the assumption that the activity coefficients for both fullerenes were independent of both concentrations:

$$\gamma(C_{60}) = \text{const}, \quad \gamma(C_{70}) = \text{const}' \quad (8)$$

C_{60} - C_{70} -1,2-DIMETHYLBENZENE

Table 5. Calculated Solubilities of C_{60} and C_{70} in 1,2-Dimethylbenzene and Measured Solubilities in the Corresponding

T, K	$s(C_{60})$, mg/mL	$s(C_{70})$, mg/mL
283	3.9	5.0
293	6.0	7.0
298	7.3	9.0
303	7.4	10.0
305	7.7	9.0
309	8.4	8.0
313	7.4	7.0
323	6.1	6.0
333	5.3	5.0
343	4.9	4.0
353	4.4	4.0
363	3.6	—
373	3.2	—
383	2.8	—
393	2.5	—
403	2.2	—
413	2.0	—

^aData from Ref. 13.

at constant temperature and varying $X_{C_{60}}$. The activity coefficients $\gamma(C_{60})$ and $\gamma(C_{70})$ were estimated from the measured solubilities of C_{70} with 1,2-dimethylbenzene, respectively. In the saturated solutions the solvent, 1,2-dimethylbenzene was taken as the standard state.

Partial solubilities of C_{60} and C_{70} in 1,2-dimethylbenzene and the solubilities of C_{60} and C_{70} in the ternary saturated liquid solutions and Gibbs free energies of formation of the phases I and II at room temperature up to 323 K for pure fullerenes and solvates are valid:

$$RT\{0.08 \cdot \ln\} X^{\text{bin}}(C_{70})/X^{\text{ter}}(C_{70}) = -\Delta G(6)$$

$$RT\{0.78 \cdot \ln\} X^{\text{bin}}(C_{70})/X^{\text{ter}}(C_{70}) = -\Delta G(7)$$

where X^{bin} and X^{ter} are solubilities in binary and ternary saturated liquid solutions, respectively. From $X^{\text{bin}}(C_{60})$, and $X^{\text{bin}}(C_{70})$, we next calculate

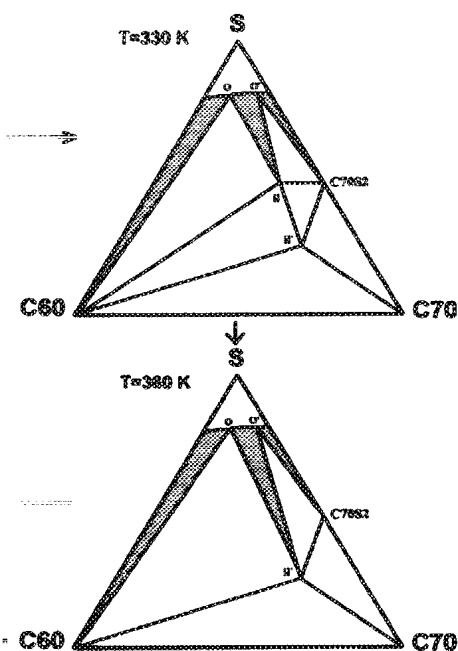


Figure 4. Phase diagram of the system C₆₀-C₇₀-1,2-

dimethylbenzene in equilibrium with the saturated liquid solutions. The regions (phase I-phase II-saturated liquid solution O'), along with the regions II, and C₇₀S₂ with their saturated liquid solutions, show the evolution of the diagram with the temperature. The decomposition of solvates at T = 323, 391, and 413 K. The sketches in Figure 4 are based on the data of the phases I and II from binary systems (2) and (3, 4) were considered to be pure, and the formation of solid solutions of the pure,

and the saturated liquid solutions (Table 5) were estimated. The activity coefficients for both fullerenes were inde-

(8)

Table 5. Calculated Solubilities of Fullerenes (Point O) in the Ternary System and Measured Solubilities in the Corresponding Binary System^a

T, K	s(C ₆₀), mg/mL	s(C ₆₀), mg/mL ^a	s(C ₇₀), mg/mL	s(C ₇₀), mg/mL ^a
283	3.9	5.0	5.4	13.1
293	6.0	7.7	6.1	14.6
298	7.3	9.3	6.5	15.6
303	7.4	10.3	6.7	—
305	7.7	9.3	6.8	—
309	8.4	8.4	7.1	—
313	7.4	7.4	7.7	18.2
323	6.1	6.1	9.3	—
333	5.3	5.3	11.4	20.7
343	4.9	4.9	13.0	—
353	4.4	4.4	13.8	21.8
363	3.6	—	14.4	—
373	3.2	—	15.9	—
383	2.8	—	17.5	—
393	2.5	—	18.4	—
403	2.2	—	17.0	—
413	2.0	—	15.8	—

^aData from Ref. 13.

at constant temperature and varying X(C₆₀) and X(C₇₀). This means that the activity coefficients γ(C₆₀) and γ(C₇₀) were equal to those in the binary systems C₆₀ and C₇₀ with 1,2-dimethylbenzene, respectively. Since the concentrations of fullerenes in the saturated solutions were rather small, the thermodynamic activity of the solvent, 1,2-dimethylbenzene was taken to be unity in all the calculations.

Partial solubilities of C₆₀ and C₇₀ in Table 5 were calculated therefore from the solubilities of C₆₀ and C₇₀ in the binary systems at different temperatures (13) and Gibbs free energies of formation of the ternary and binary solid solvates. From room temperature up to 323 K for point O of the ternary diagram the following equations are valid:

$$RT\{0.08 \cdot \ln\{X^{\text{bin}}(\text{C}_{70})/X^{\text{ter}}(\text{C}_{70})\} + 0.92 \cdot \ln\{X^{\text{bin}}(\text{C}_{60})/X^{\text{ter}}(\text{C}_{60})\}\} = -\Delta G \quad (6) \quad (9)$$

$$RT\{0.78 \cdot \ln\{X^{\text{bin}}(\text{C}_{70})/X^{\text{ter}}(\text{C}_{70})\} + 0.22 \cdot \ln\{X^{\text{bin}}(\text{C}_{60})/X^{\text{ter}}(\text{C}_{60})\}\} = -\Delta G \quad (7) \quad (10)$$

where X^{bin} and X^{ter} are solubilities in molar fractions of fullerenes in the binary and ternary saturated liquid solutions, respectively. Knowing ΔG (6), ΔG (7), X^{bin}(C₆₀), and X^{bin}(C₇₀), we next calculate X^{ter}(C₆₀) and X^{ter}(C₇₀) from Equations

(9) and (10). At temperatures above 323 K Equation (9) is no longer valid and has to be replaced by the simple relation $X^{\text{bin}}(\text{C}_{60}) = X^{\text{ter}}(\text{C}_{60})$, etc. The solubilities of C_{60} and C_{70} , $s(\text{C}_{60})$ and $s(\text{C}_{70})$, calculated from $X^{\text{ter}}(\text{C}_{60})$ and $X^{\text{ter}}(\text{C}_{70})$, respectively, are presented in Table 5.

As it is seen from Table 5, for fullerene mixtures with molar ratios of C_{60} to C_{70} from 11.5 to 0.28, the maximum solubility of C_{60} was reached near the temperature of incongruent melting of phase I. For C_{70} , maximum solubility must be reached at 391 K. The maximum ratio of C_{70} to C_{60} in the liquid solution could be obtained also at $T = 391$ K. The data in Table 5 demonstrate, that for the so-called "extract," the commercially important solid mixture with the molar ratio of C_{60} to C_{70} near 5:1, the same ratio in the saturated liquid solution must change from 1:0.76 to 1:6.3 with an increase in the temperature from 298 K up to 393 K. Thermodynamic equations, based on the conditions of phase equilibrium (see the Appendix) predicted the appearance of the solubility maximums or/and breakpoints for both C_{60} and C_{70} at the incongruent melting points of phases I and II, respectively. The equations are similar to those for the binary systems.

Solubility Measurements

Room temperature solubility measurements were performed to check the validity of the assumption (8). The results are presented in Table 6. The accuracy estimated was 10%.

As is seen in Table 6, the solubility of C_{60} in the unsaturated solution of C_{70} in 1,2-dimethylbenzene within the experimental error coincided with the solubility of C_{60} in the neat solvent. Our data on the latter solubility were in good accord with the literature value (13) (see Table 5). However, measurements performed with different ternary solid samples gave solubilities of C_{60} and C_{70} which were substantially higher than those predicted in Table 5. In case of C_{60} the solubility was 1.7 times in excess of the room temperature solubility of this fullerene in the

Table 6. Measured Solubilities of C_{60} and C_{70} at 298 K

Sample, $\text{C}_{60}:\text{C}_{70}$	Solvent	$s(\text{C}_{60})$, mg/mL	$s(\text{C}_{70})$, mg/mL
C_{60}	1,2-Dimethylbenzene	9.5	—
C_{60}	9.13 mg/ml C_{70} in 1,2-dimethylbenzene	10.1	—
5.09:1 ^a	1,2-dimethylbenzene	15.9	15.6
1:1	1,2-dimethylbenzene	13.2	14.9

^a"extract": mixture of C_{60} and C_{70} with molar ratio $\text{C}_{60}/\text{C}_{70}$ 5.09 and admixture of high fullerenes.

binary system of C_{60} with 1,2-dimethylbenzene could be suggested that the salt-in effect could be the formation of the metastable phase. Further work is needed to understand the nature of this effect.

CONCLUSION

In this study the formation of ternary solvates of 1,2-dimethylbenzene was confirmed. One of the solvates (phase II) on the crystal structure of the binary system (phase I) is different from the binary system. The Gibbs free energies of the ideal mixing and the stability of the ternary solid phase in equilibrium with the mixture of phases I and II in the 0.22 mole fraction of C_{60} in the solvent.

Formation of the binary solvated fullerene complexes, appeared to be the main reason for the properties of the fullerene in the solvent. The solubility of fullerene mixtures in the solvents. It brought about a complicated picture of the solubility of C_{60} to C_{70} in the saturated liquid solution. The salt-in effect was found in the solubility of fullerenes in the saturated solutions.

APPENDIX

The thermodynamic equations for the calculation of solubilities (molar fractions) $X(\text{C}_{60})$ and $X(\text{C}_{70})$ for the binary systems C_{60} -solvent or C_{70} -solvent and for the ternary system of phase equilibrium, e.g., for the ternary system C_{60} - C_{70} -solvent

$$\mu(\text{phase I}) = x' \cdot \mu(\text{C}_{60}, \text{ in the solvent}) + (1 - x') \cdot \mu(\text{solvent})$$

$$\mu(\text{phase II}) = x'' \cdot \mu(\text{C}_{60}, \text{ in the solvent}) + (1 - x'') \cdot \mu(\text{solvent})$$

where x' and x'' are fullerene molar fractions in the phases. In our case $x' = 0.92$ and $x'' = 0.22$. To T , $X(\text{C}_{60})$, and $X(\text{C}_{70})$, one obtains $dX(\text{C}_{70})/dT$. Assuming that in the dilute solution

Equation (9) is no longer valid and has to be replaced by $X^{\text{ter}}(C_{60})$, etc. The solubilities of C₆₀ and C₇₀ in the ternary system are denoted by $X^{\text{ter}}(C_{60})$ and $X^{\text{ter}}(C_{70})$, respectively.

Fullerene mixtures with molar ratios of C₆₀ to C₇₀ were studied. The solubility of C₆₀ was reached near the phase I. For C₇₀, maximum solubility must be reached at a molar ratio of C₇₀ to C₆₀ in the liquid solution. The data in Table 5 demonstrate, that for the most important solid mixture with the molar ratio of C₆₀ to C₇₀ in the saturated liquid solution must be reached in the temperature from 298 K up to 300 K on the conditions of phase equilibrium. The dependence of the solubility maximums or/and congruent melting points of phases I and II on the conditions of phase equilibrium are different from those for the binary systems.

Measurements

Measurements were performed to check the results. The data are presented in Table 6. The accuracy of the measurements is high.

The solubility of C₆₀ in the unsaturated solution of C₇₀ was studied. The experimental error coincided with the solubility of C₆₀ in the latter solution. The results are in good accord with the data in Table 5. However, measurements performed at different temperatures of the solubilities of C₆₀ and C₇₀ which were presented in Table 5. In case of C₆₀ the solubility in the saturated liquid solution at different temperatures of this fullerene in the saturated liquid solution.

Solubilities of C₆₀ and C₇₀ at 298 K

	s(C ₆₀), mg/mL	s(C ₇₀), mg/mL
Phase I	9.5	—
Phase II	10.1	—
Phase III	15.9	15.6
Phase IV	13.2	14.9

Molar ratio C₆₀/C₇₀ 5.09 and admixture of high

solubility of C₆₀ with 1,2-dimethylbenzene. This result was reproducible. It could be suggested that the salt-in effect took place. An alternative explanation could be the formation of the metastable solid phases in the ternary system. More work is needed to understand the nature of the unexpectedly high solubilities.

CONCLUSIONS

In this study the formation of two ternary compounds of C₆₀, C₇₀ with 1,2-dimethylbenzene was confirmed. One of them (phase I) is a solid solution based on the crystal structure of the binary solvated crystal C₆₀S₂. The second crystal structure (phase II) is different from those of the binary solvates of C₆₀ or C₇₀. Gibbs free energies of the ideal mixing of the binary phases C₆₀S₂ and C₇₀S₂ gave a reasonable estimation for the stability of the phases I and II. At room temperature the ternary solid phase in equilibrium with the liquid solution was a mechanical mixture of phases I and II in the 0.22 ≤ x(C₆₀) ≤ 0.92 concentration range.

Formation of the binary solvated crystals, some relatively weak bounded Van der Waals complexes, appeared to be the crucial factor determining the dissolution properties of the fullerene in the solvent (8). The additional impact of ternary solvates on the solubility of fullerene mixtures is comparable with those of the binary solvates. It brought about a complicated temperature dependence of a molar ratio of C₆₀ to C₇₀ in the saturated liquid solutions. Surprisingly, some evidence of the C₆₀-C₇₀ salt-in effect was found in the solutions under study. Low concentrations of fullerenes in the saturated solutions made this effect hard to explain.

APPENDIX

The thermodynamic equations for the temperature dependence of partial solubilities (molar fractions) X(C₆₀) and X(C₇₀) can be obtained in the same way as for the binary systems C₆₀-solvent or C₇₀-solvent (7,8). Starting from the conditions of phase equilibrium, e.g., for the triangle I-II-O (Fig. 4),

$$\begin{aligned} \mu(\text{phase I}) &= x' \cdot \mu(C_{60}, \text{ in the solution}) \\ &+ (1 - x') \cdot \mu(C_{70}, \text{ in the solution}) + 2\mu(S) \end{aligned}$$

$$\begin{aligned} \mu(\text{phase II}) &= x'' \cdot \mu(C_{60}, \text{ in the solution}) \\ &+ (1 - x'') \cdot \mu(C_{70}, \text{ in the solution}) + 2\mu(S), \end{aligned}$$

where x' and x'' are fullerene molar fractions of C₆₀ in the equilibrium solid phases. In our case $x' = 0.92$ and $x'' = 0.22$. After differentiation with respect to T, X(C₆₀), and X(C₇₀), one obtains the expressions for both dX(C₆₀)/dT and dX(C₇₀)/dT. Assuming that in the diluted liquid solutions

1. the equation $(\partial\mu/\partial X)_{p,T} = RT/X$ is valid for the solutes,
2. the chemical potential μ of a solvent is equal to μ of a pure liquid solvent,
3. the concentration of fullerenes in the solid solvates is well over the saturated concentration in the liquid solution, one gets for the compositions inside the triangle

$$\frac{d \ln X_{C_{60}}}{dT} = \frac{1}{RT^2} \left\{ \Delta_{\text{sol}}H_{C_{60}} - \frac{(1-x'') \cdot \Delta_f H_I - (1-x') \cdot \Delta_f H_{II}}{(x' - x'')} \right\}$$

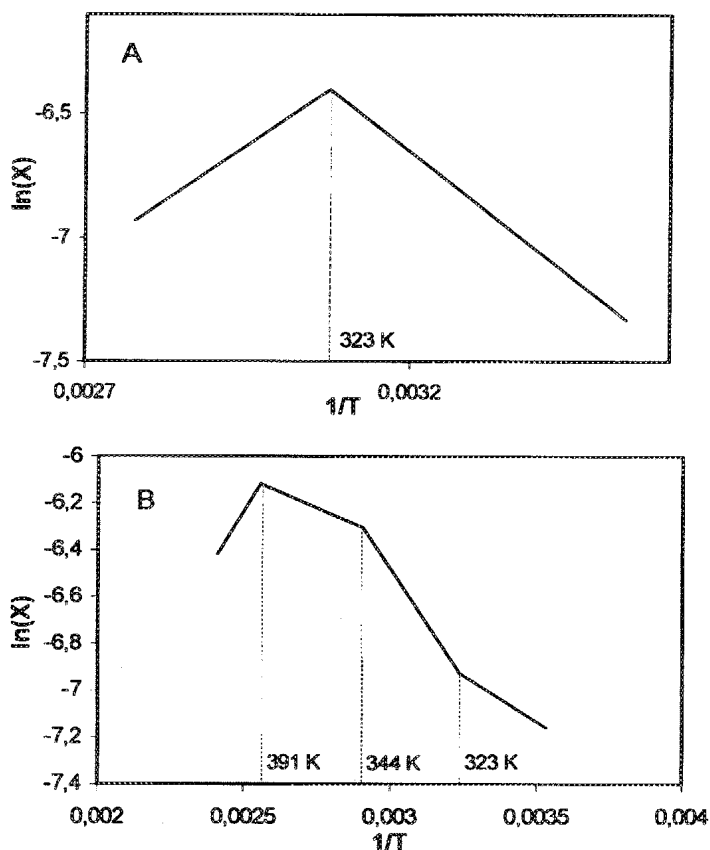


Figure 5. A. Schematic temperature dependence of the solubility of C_{60} , $\ln(X)$, in the ternary system C_{60} - C_{70} -1,2-dimethylbenzene. B. Schematic temperature dependence of the solubility of C_{70} , $\ln(X)$, in the ternary system C_{60} - C_{70} -1,2-dimethylbenzene.

$$\frac{d \ln X_{C_{70}}}{dT} = \frac{1}{RT^2} \left\{ \Delta_{\text{sol}}H_{C_{70}} \right\}$$

where $\Delta_{\text{sol}}H_{C_{60}}$ and $\Delta_{\text{sol}}H_{C_{70}}$ are pure fullerenes into the saturated formation of the phases I and II respectively, and $I = (C_{60})_x(C_{70})_{1-x}$ solvates, which are in equilibrium with

Similar equations could be written for the ternary system C_{60} - C_{70} -1,2-dimethylbenzene. For $T = 323, 344, \text{ or } 393 \text{ K}$ one set of equations would appear for the next three-phase region. Maximum values would appear at these temperatures. These values are schematically presented in Figure 5.

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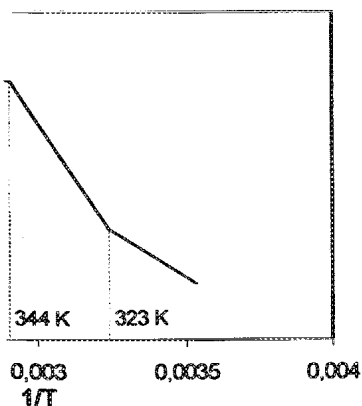
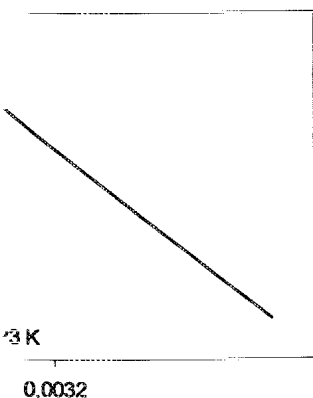
REFERENCES

1. Beck, M.T.; Mandi G. Fullerenes and Nanotubes. *Chemical Reviews* 1998, 78, 1367-1400.
2. Sivaraman, N.; Dhamodaran, S.; Rao, P.R.; Mathews, C.K. In *Fullerenes and Nanotubes*; Electrochemical Society, 1994; pp 1-10.
3. Doome, R.J.; Dermaut, S.; Fontijn-Tekampel, M. *Sci. Technol.* 1997, 5, 1593.
4. Olofsson, G.; Wadso, I.; Ruoff, R. Eds.; *Chemistry and Physics of Fullerenes*; Ruoff, R. Eds.; Electrochemical Society, 1994; pp 1-10.
5. Michaud, F.; Barrio, M.; Tosca, M. *Fullerene Sci. Technol.* 1997, 5, 1593.
6. Nagano, Y.; Tamura, T. *Chem. Lett.* 1997, 126, 1593.
7. Korobov, M.V.; Mirakian, A.L.; I.S.; Slovokhotov, Yu.L.; Smith, D. *B* 1998, 102, 3712.

$\ln X$ is valid for the solutes,
solvent is equal to μ of a pure liquid

in the solid solvates is well over the satu-
d solution, one gets for the compositions

$$\frac{-x'' \cdot \Delta_f H_I - (1-x') \cdot \Delta_f H_{II}}{(x' - x'')}$$



dependence of the solubility of C₆₀. $\ln(X)$, in the
B. Schematic temperature dependence of the
C₆₀-C₇₀-1,2-dimethylbenzene.

$$\frac{d \ln X_{C_{70}}}{dT} = \frac{1}{RT^2} \left\{ \Delta_{sol} H_{C_{70}} - \frac{(x') \cdot \Delta_f H_{II} - (x'') \cdot \Delta_f H_I}{(x' - x'')} \right\}$$

where $\Delta_{sol} H_{C_{60}}$ and $\Delta_{sol} H_{C_{70}}$ are partial molar enthalpies of dissolution of solid pure fullerenes into the saturated solution; $\Delta_f H_I$ and $\Delta_f H_{II}$ are enthalpies of formation of the phases I and II from the pure fullerenes and liquid solvent, respectively, and I = (C₆₀)_x(C₇₀)_{1-x}S_m, and II = (C₆₀)_{x''}(C₇₀)_{1-x''}S_m, solid ternary solvates, which are in equilibrium with liquid solution of fullerenes.

Similar equations could be written for every three-phase equilibrium within the ternary system C₆₀-C₇₀-1,2-dimethylbenzene. At the transition temperatures $T = 323, 344, \text{ or } 393 \text{ K}$ one set of equations should be replaced by another set valid for the next three-phase region. Maxima and breakpoints on the curves of solubility would appear at these temperatures. $\ln X(C_{60})$ and $\ln X(C_{70})$ vs. $1/T$ dependencies are schematically presented in Figure 5.

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REFERENCES

1. Beck, M.T.; Mandi G. *Fullerene Sci. Technol.* **1997**, *5*, 1593.
2. Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T.G.; Vasudeva Rao, P.R.; Mathews, C.K. In *Fullerenes Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*. Kadish, K., Ruoff, R., Eds.; Electrochemical Society, 1994; Vol. 94-24, 156.
3. Doome, R.J.; Dermaut, S.; Fonseca, A.; Hammida, M.; Nagy, J.B. *Fullerene Sci. Technol.* **1997**, *5*, 1593.
4. Olofsson, G.; Wadso, I.; Ruoff, R.S. In *Fullerenes Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Kadish, K.; Ruoff, R. Eds.; Electrochemical Society, 1996, Vol. 96-10, 17.
5. Michaud, F.; Barrio, M.; Toscani, S.; Agafonov, V.; Szwarc, H.; Ceolin, R. *Fullerene Sci. Technol.* **1997**, *5*, 1645.
6. Nagano, Y.; Tamura, T. *Chem. Phys. Lett.* **1996**, *252*, 362.
7. Korobov, M.V.; Mirakian, A.L.; Avramenko, N.V.; Valcev, E.F.; Neretin, I.S.; Slovokhotov, Yu.L.; Smith, A.; Olofsson, G.; Ruoff, R. *J. Phys. Chem. B* **1998**, *102*, 3712.

8. Korobov, M.V.; Mirakyan, A.L.; Avramenko, N.V.; Olofsson, G.; Smith, A.L.; Ruoff, R.S. *J. Phys. Chem. B* **1999**, *103*, 1339.
9. Jansen, M.; Kneip, K.; Waidman, G. *Fullerene Sci. Technol.* **1997**, *5*, 1645.
10. Jansen, M.; Waidman, G., *Z. Anorg. Allg. Chem.* **1995**, *621*, 14.
11. Sai baba, M.; Lakshmi Narasimhan, T.S.; Balasubramanian, R.; Sivaraman, N.; Mathews, C.K. *J. Phys. Chem.* **1994**, *98*, 1333.
12. Korobov, M.V.; Skokan, E.V.; Dorozhko, P.A.; Homich, L.; Kurskaya A. In *Fullerenes Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*. Kadish, K.; Ruoff, R. Eds.; Electrochemical Society, 1994, Vol. 94-24, 1595.
13. Zhou, X.; Liu, J.; Jin, Z.; Gu, Z.; Wu, Y.; Sun, Y. *Fullerene Sci. Technol.* **1997**, *5*, 285.

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