TERNARY SYSTEM OF C\textsubscript{60} AND C\textsubscript{70} 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 C\textsubscript{60}-C\textsubscript{70}-1,2-dimethylbenzene up to the boiling point of the solvent. Formation of the two ternary phases was confirmed. Partial solubilities of C\textsubscript{60} and C\textsubscript{70} were measured and calculated.

INTRODUCTION

Extraction and fractional crystallization could play a certain role in the production of the pure fullerenes C\textsubscript{60} and C\textsubscript{70}. 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 C₆₀ and C₇₀ with different organic solvents have been extensively studied in recent years. The solubility of C₆₀ at room temperature was measured in more than 100 solvents (1). Much less is known about the solubility of C₇₀ (2,3). Partial solubilities of C₆₀ and C₇₀ 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 C₆₀ forms the stoichiometric solvated crystal C₆₀·2C₈H₁₀. The enthalpy of decomposition of this crystal was found to be 31 ± 2 kJ/mol of C₆₀ (8). In the binary system of C₇₀ 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 C₇₀, respectively. The latter enthalpy corresponded to the decomposition of the solvated crystal composed of a C₇₀·2C₈H₁₀ 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 C₆₀ with C₇₀ have been reported.

The only example of a ternary system studied was C₆₀ and C₇₀ with cyclohexane (9). X-ray analysis confirmed the formation of the solid solvate solutions C₆₀/C₇₀·12C₈H₁₂ 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 C₇₀·12C₈H₁₂ and C₆₀·12C₈H₁₂ had isomorphous crystal structures (10).

In the present study an effort was made to examine ternary system of C₆₀ and C₇₀ 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 C₆₀ and C₇₀.

**EXPERIMENTAL**

Samples of C₆₀ were from Bucky USA and MER Ltd. (99.9% mol purity) and C₇₀ 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.

**C₆₀-C₇₀-1,2-DIMETHYLBENZENE**

Thirteen heterogeneous (solid different molar ratios of C₆₀ to C₇₀ an solvent to fullerenes were less than 10 than 98% of fullerenes were kept in the solution. The samples were prepared by mixing weighed aluminum DSC pans and then sealing the way of preparation included complete and C₇₀ in 1,2-dimethylbenzene at room precipitated from the solution by evaporation at room temperature. For accelerating removed by the air flow in 2–3 h. The solid + liquid sample was then put into the scanning (procedure B).

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

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

Powder X-ray diffraction data w CuKα. The samples were prepared according to the Ternary and binary saturated liquid were prepared by stirring in a thermos. The solution was stirred until it was at equilibrium. The solubilities of C₆₀ and C₇₀ were spectrophotometrically using prelimin
C_{60}-C_{70}-1,2-DIMETHYLBENZENE

Thirteen heterogeneous (solid + saturated liquid solution) samples with different molar ratios of C_{60} to C_{70} and to the solvent were studied. Molar ratios of solvent to fullerenes were less than 1 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 C_{60}, C_{70}, 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 C_{60} and C_{70} 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 samples were left to stand at room temperature or at T = 260 K in the refrigerator for a period of 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 C_{60} and C_{70} 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, CuKα. 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 ±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 C_{60} and C_{70} 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<sub>60</sub>-C<sub>70</sub>-1,2-dimethylbenzene x(C<sub>60</sub>)-fullerene molar fraction ν(C<sub>60</sub>)/[ν(C<sub>60</sub>) + ν(C<sub>70</sub>)] in the sample.

Results

Formation of the

Ternary solid samples with different molar ratios were examined. Typical DSC scans in Figure 1 show two waves in the case of ternary mixtures. The 333.6 nm molar extinction coefficients and ε(C<sub>70</sub>) = 29,968 ± 649 M<sup>-1</sup> cm<sup>-1</sup> for C<sub>70</sub> were derived from SPECORD ultraviolet-visible spectra of fullerenes in the concentration range 8.21 · 10<sup>-5</sup> M to C<sub>70</sub>. Molar extinction coefficients for C<sub>60</sub> to C<sub>70</sub> were additionally checked.

Table 1. DSC Peaks in the Ternary System C<sub>60</sub>-C<sub>70</sub>-1,2-Dimethylbenzene

<table>
<thead>
<tr>
<th>Temperature of the peak (onset), K</th>
<th>Temperature of the peak (maximum), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>323 ± 3</td>
<td>329 ± 3</td>
</tr>
<tr>
<td>274 ± 3</td>
<td>283 ± 3</td>
</tr>
<tr>
<td>344 ± 6</td>
<td>350 ± 6</td>
</tr>
<tr>
<td>391 ± 3</td>
<td>396 ± 3</td>
</tr>
<tr>
<td>310 ± 1</td>
<td>320 ± 2</td>
</tr>
<tr>
<td>365 ± 1</td>
<td>368.7 ± 0.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> See text for more discussion.

<sup>b</sup> Data from Ref. 8.
two waves in the case of ternary liquid solutions. Analytical wavelengths \( \lambda_1 = 333.6 \text{ nm} \) \[ \varepsilon(C_{60}) = 44,712 \pm 542 \text{ M}^{-1} \text{ cm}^{-1} \]
and \[ \varepsilon(C_{70}) = 29,968 \pm 649 \text{ M}^{-1} \text{ cm}^{-1} \] and \( \lambda_2 = 485.6 \text{ nm} \) \[ \varepsilon(C_{70}) = 17,630 \pm 424 \text{ M}^{-1} \text{ cm}^{-1} \] and \( \varepsilon(C_{60}) \approx 0 \) were used. Measurements were taken with the SPECORD ultraviolet-visible instrument. Calibration curves were prepared for fullerenes in the concentration ranges \((0.74–5.17) \cdot 10^{-5} \text{ M}\) for \( C_{60} \) and \((1.65–8.21) \cdot 10^{-5} \text{ M}\) for \( C_{70} \). Molar extinction coefficients were constant within the standard deviations shown above. The reliability of the measured ratio of solubilities \( C_{60} \) to \( C_{70} \) 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 \( C_{60} \) to \( C_{70} \) 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 \( C_{60}-C_{70}-1,2\)-dimethylbenzene are presented in Table 1 along with the literature data on the binary systems \( C_{60}-1,2\)-dimethylbenzene and \( C_{70}-1,2\)-dimethylbenzene (8). As is seen from Table 1, peaks

<table>
<thead>
<tr>
<th>Temperature of the peak (onset), K</th>
<th>Temperature of the peak (maximum), K</th>
<th>The Process Assumed⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>323 ± 3</td>
<td>329 ± 3</td>
<td>( (C_{60})<em>x(C</em>{70})<em>{1-x}S_2 (s, I) = x'C</em>{60} (s) + (1 - x')C_{70} (s) + nS ) (liq)</td>
</tr>
<tr>
<td>274 ± 3</td>
<td>283 ± 3</td>
<td>( (C_{60})<em>x(C</em>{70})<em>{1-x}S_2 (s, I) = (1 - \frac{m}{n})C</em>{60} (s) + \frac{m}{n}S ) (liq)</td>
</tr>
<tr>
<td>344 ± 6</td>
<td>350 ± 6</td>
<td>( (C_{60})<em>x(C</em>{70})<em>{1-x}S_2 (s, II) = (C</em>{60})<em>x(C</em>{70})_{1-x}S_2 (s, II) + (m - k)S ) (liq)</td>
</tr>
<tr>
<td>391 ± 3</td>
<td>396 ± 3</td>
<td>( (C_{60})<em>x(C</em>{70})<em>{1-x}S_2 (s, II') = x''(C</em>{60}) (s) + (1 - x'')C_{70} (s) + kS ) (liq)</td>
</tr>
<tr>
<td>310 ± 1</td>
<td>320 ± 2</td>
<td>( C_{60}S_2 (s) = C_{60} (s) + 2S ) (liq)³</td>
</tr>
<tr>
<td>365 ± 1</td>
<td>368.7 ± 0.8</td>
<td>( C_{70}S_2 (s) = C_{70} (s) + 2S ) (liq)³</td>
</tr>
</tbody>
</table>

⁹ See text for more discussion.

³ Data from Ref. 8.
found in the ternary system are different from peaks observed earlier in the binary systems C\textsubscript{60}-1,2 dimethylbenzene and C\textsubscript{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\textsubscript{70} depended on the initial composition of the sample and reached its maximum at the C\textsubscript{60}:C\textsubscript{70} molar ratio close to 1:3. With the samples containing more C\textsubscript{70} the peak at 365 K (onset) was observed, which corresponded to decomposition of the binary solvate C\textsubscript{70} \cdot 2C\textsubscript{x}H\textsubscript{10} (C\textsubscript{70}S\textsubscript{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 \pm 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\textsubscript{60}:C\textsubscript{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\textsubscript{60}:C\textsubscript{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 \pm 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\textsubscript{60} was practically equal to the enthalpy of decomposition of the binary solvate C\textsubscript{60} \cdot 2C\textsubscript{x}H\textsubscript{10} (C\textsubscript{60}S\textsubscript{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\textsubscript{60} to C\textsubscript{70} are presented in Figure 2. X-ray data confirmed the formation of the ternary phases. It could be supposed that the samples rich with C\textsubscript{60} [e.g., \( x(C_{60}) = 0.86 \) in Figure 2] structure of the binary solvate C\textsubscript{60}S\textsubscript{2} [x] diffraction it was not possible to care for which phase I was stable, though it was \( x(C_{60}) = 0.86 \) was phase I. Parameters are presented in Table 2. The apparent C\textsubscript{70} content in the solid phase \( x(C_{60}) \) of another ternary phase with a crystal solvates \( x(C_{60}) = 1 \) and \( x(C_{70}) = 1 \) in

**Determination of the Comp**

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

- **Phase I**, a solid solution with a lower endotherm at \( T = 323 \pm 3 \) K corresponding to the formation of a certain quantity of the other (it is clear that the mole fraction of C\textsubscript{60} liquid solution [reaction (1)] or with the solid and liquid solution (practically pure C\textsubscript{60}).

*Here and below \( x(C_{60}) \), fullerene molar \( v(C_{60})/v(C_{60}) + v(C_{70}) \).
from peaks observed earlier in the binary $\gamma_7$-1,2 dimethylbenzene.

$T = 391 \pm 3 \text{ K}$

well above those for the effects observed with the samples of all the compositions 1, the initial composition at the C$_{60}$:C$_{70}$ molar ratio close to 1, the peak at 365 K (onset) was observed, f the binary solvate C$_{70}$ · 2C$_8$H$_{10}$ (C$_{70}$S$_2$), th sides of the 1:3 composition proved the h peak at 391 ± 3 K was easily detected

$T = 344 \pm 6 \text{ K}$

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$T = 323 \pm 3 \text{ K}$

or the samples rich in C$_{60}$ was practically f the binary solvate C$_{60}$ · 2C$_8$H$_{10}$ (C$_{60}$S$_2$), n that of the corresponding binary solvate. amplex A.

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 $T = 323 \pm 3 \text{ K}$ 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

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*Here and below $x(C_{60})$, fullerene molar fraction in the ternary system, is equal to $v(C_{60})/v(C_{60}) + v(C_{70})$.
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Table 2. The Parameters of the Elementary Cell of the Binary Solvate and Phase I

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>C</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>V</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}S_2</td>
<td>15.33 (1)</td>
<td>13.08 (4)</td>
<td>10.01 (3)</td>
<td>90</td>
<td>99.4 (1)</td>
<td>90</td>
<td>1980</td>
<td>2</td>
</tr>
<tr>
<td>Phase I</td>
<td>15.46 (1)</td>
<td>13.20 (2)</td>
<td>10.21 (1)</td>
<td>90</td>
<td>99.87 (8)</td>
<td>90</td>
<td>2053</td>
<td>2</td>
</tr>
</tbody>
</table>

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

\[(C_{60})_x(C_{70})_1-xS_n (s, I) \rightarrow 1 - \frac{x}{1 - x'} \] C_{60} (s)

\[+ \frac{1 - x'}{1 - x''} (C_{60})_x(C_{70})_1-xS_m (s, II) \]

\[+ \left\{ n - m \frac{1 - x'}{1 - x''} \right\} S (liq) \]  

(1)

\[(C_{60})_x(C_{70})_1-xS_n (s, I) \rightarrow x'C_{60} (s) + (1 - x')C_{70} (s) + nS (liq) \]  

(2)

Phase II, with the molar ratio of C_{60} to C_{70} 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 C_{60} to C_{70} in phase II below and above 344 K was considered to be the same. The endotherm near 274 \( \pm 3 \) 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).

\[(C_{60})_x(C_{70})_1-xS_m (s, II) \rightarrow (C_{60})_x(C_{70})_1-xS_k (s, II') \]

\[+ (m - k)S (liq) \]  

(3)

\[(C_{60})_x(C_{70})_1-xS_k (s, II') \rightarrow x''C_{60} + (1 - x'')C_{70} + kS (liq) \]  

(4)

Samples with the molar ratio of C_{60} and C_{70} 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 \( T = 323 \pm 3 \text{ K} \), \( T = 344 \pm 6 \text{ K} \), \( T = 391 \pm 3 \text{ K} \) to the fullerene molar fraction of C_{60} in the sample, \( x(C_{60}) = \nu(C_{60})/\{\nu(C_{60}) + \nu(C_{70})\} \). For \( \Delta H (323 \text{ K}) \) one gets:

\[\Delta H (323 \text{ K})/\{\nu(C_{60}) + \nu(C_{70})\} = \Delta H^0(323 \text{ K}) \cdot \{x(C_{60}) - x''(C_{60})\}/\{x'(C_{60}) - x''(C_{60})\} \]  

(5)

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 C_{60} in phases I and II, respectively. The least-square treatment of the dependence \( \Delta H (323 \text{ K})/\{\nu(C_{60}) + \nu(C_{70})\} \) vs. \( x(C_{60}) \) for

\[y = 42.6x \]

\[R^2 = 0.99 \]

Figure 3. a. Dependence of the enthalpy versus fullerene molar fraction of C_{60} in the effect at 391 K per mole of fullerenes versus
\[ a \]

$y$ Cell of the Binary Solvate and Phase I

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$V$</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>99.4 (1)</td>
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<td>1980</td>
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</tr>
<tr>
<td>90</td>
<td>99.87 (8)</td>
<td>90</td>
<td>2053</td>
<td>2</td>
</tr>
</tbody>
</table>

...under the conditions of our DSC c... below).

\[
\begin{align*}
\frac{-x'}{-x''} & \left\{ C_{60} \right\} (s) \\
\frac{x'}{x''} & \left\{ C_{60} \right\} (s) (C_{70})_{1-x'}S_m \left( s, \text{II} \right) \\
\frac{m - x'}{m - x''} & S \left( \text{liq} \right) \\
\frac{-kS}{m (C_{60}) + kS \left( \text{liq} \right)} & \\
(1 - x')C_{70} (s) + nS (\text{liq}) & \\
\end{align*}
\]

...to $C_{70}$ close to 1:3. Endotherms at $T = ... deduced to the two-step loss of solvent from...ilar ratio of $C_{60}$ to $C_{70}$ in phase II below...e same. The endotherm near 274 ± 3 K...old even more solvent molecules. The...ion with enthalpies measured at 391 K...les was changed (see Fig. 1).

\[
\begin{align*}
\frac{x'}{x''} & \left\{ (C_{70})_{1-x'}S_k \left( s, \text{II} \right) \right\} \\
-kS & \left( \text{liq} \right) \\
\frac{1 - x''}{1 - x''} & + C_{70} + kS \left( \text{liq} \right) \\
\end{align*}
\]

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

The measured enthalpies $\Delta H$ (323 K),... at $T = 323 \pm 3$ K, $T = 344 \pm 6$ K,..ion of $C_{60}$ in the sample, $x(C_{60}) = \nu(C_{60})/\nu(C_{60})$...gets:

\[
\frac{\nu(C_{60})}{\nu(C_{60})} - x''(C_{60}) \right\} \\
\]

reaction (1) or (2), $x'(C_{60})$ and $x''(C_{60})$...phases I and II, respectively. The least-

Figure 3. a. Dependence of the enthalpy of the effect at 323 K per mole of fullerenes versus fullerene molar fraction of $C_{60}$ in the sample. b. Dependence of the enthalpy of the effect at 391 K per mole of fullerenes versus fullerene molar fraction of $C_{60}$ 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 \( \Delta H (391 \text{ K})/\{\nu(C_{70})\} \) 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 \( \Delta H (391 \text{ K})/\{\nu(C_{60}) + \nu(C_{70})\} \) 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 \( \Delta H^0(323 \text{ K}), \Delta H^0(344 \text{ K}), \text{ and } \Delta H^0(391 \text{ K}) \) 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_{8}H_{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

<table>
<thead>
<tr>
<th>Phase</th>
<th>( T, \text{ K} )</th>
<th>( \Delta H ) (2), ( \text{kJ/mol} )</th>
<th>( T_1, \text{ K} )</th>
<th>( \Delta H ) (3), ( \text{kJ/mol} )</th>
<th>( T_2, \text{ K} )</th>
<th>( \Delta H ) (4), ( \text{kJ/mol} )</th>
<th>( x(C_{60})^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>323 ± 3</td>
<td>31 ± 2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>—</td>
<td>—</td>
<td>344 ± 6</td>
<td>8.6 ± 1.0</td>
<td>391 ± 3</td>
<td>16.8 ± 1.0</td>
<td>( x' = 0.92 \pm 0.03 )</td>
</tr>
</tbody>
</table>

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

\( a \) Phase I: \((C_{60})_{0.22}(C_{70})_{0.78}S_m\); 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 \( 274 \text{ K} < T < 344 \text{ K} \).
C_{60} in phase II. Reaction (2) rather than reaction process for phase I, since a slight\(^{/i} \nu(C_{70})\) on \(x(C_{60})\) was observed. With \(x\) lower. It means that C\(_{70}\) from phase I composition. It should be emphasized that the decomposition reaction was chosen.

\[ \Delta H(391 K) / (\nu(C_{60}) + \nu(C_{70})) \] 

The average according to DSC data, phase I existed in

\( x''(C_{60}) \) one easily gets \( \Delta H^\circ(323 K) \), correspond to phase reactions (2), (3), I into the ternary solvates, was determined the same runs, the DSC peak corresponding (\( T = 248 K \)) was measured, after the os solvates. In this way the amount of extra reacted with fullerene was determined.

\( \nu \) of fullerene and solvent in the samples, in the solvates were estimated. Measure the complete composition of phase I \( \nu \) of fullerene which coincided with the \( \nu \). The amount of solvent in phase II was \( x_0 \) below 274 K. At this temperature the amount of solvent in phase II above K could be estimated only roughly. The ith the enthalpies and temperatures of the presented in Table 3.

and Compositions of the Ternary Phases

\[ \Delta H (4), \] 
\[ -T_2, K, \] 
\[ \nu, \] 
\[ x''' = 0.92 \pm 0.03 \] 
\[ 0.92 \pm 0.03 \] 
\[ 1.0 \] 
\[ 1.0 \] 
\[ 16.8 \pm 1.0 \] 
\[ 16.8 \pm 1.0 \] 
\[ 0.22 \pm 0.01 \] 
\[ x'' = 0.22 \pm 0.01 \] 
the ternary phases.

\( C_{60}x_{0.22}C_{70}x_{0.78}Sm \), where \( m = 4 \) at \( T \leq

==

\begin{table}
\centering
\caption{Ternary Phase Diagram for the System \( C_{60}C_{70}1,2\text{-dimethylbenzene} \)
\begin{tabular}{|c|c|c|c|}
\hline
Reaction & \( \Delta H \), kJ/mol & \( \Delta S \), J/mol K & Ideal Mixing
\hline
0.92 \( C_{60}S_2 + 0.08 C_{70}S_2 \) = phase I (6) & -0.7 & 1.1 & 2.1
\hline
0.22 \( C_{60}S_2 + 0.78 C_{70}S_2 \) = phase II (7) & -0.6 & 3.6 & 4.4
\hline
\end{tabular}
\end{table}

Thermodynamic Consideration

In Table 4 the enthalpies and the entropies of mixing of the binary solvates \( C_{60}S_2 \) and \( C_{70}S_2 \) 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, \( \Delta \), \( \Delta S \) and \( \Delta H \) 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 \( C_{60}S_2 \). X-ray data for phase I resembled those for the binary phase. The volume of the cell in phase I is larger, since the \( C_{70} \) unit is larger, compared to the \( C_{60} \) sphere (see Table 2). The Gibbs free energy of reaction (6) is \(-1.3\) kJ/mol at \( T = 310 \) K.

X-ray diffraction patterns for phase II are different from those of \( C_{70}S_2 \) or \( C_{60}S_2 \) 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 \( C_{60}S_2 \) and 0.78 \( C_{70}S_2 \) \((-1.7 \) and \(-1.3\) kJ/mol, respectively, at \( T = 310 \) 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 \( C_{60}C_{70} \). The molar ratio of \( C_{60}/C_{70} = 0.22 \) in phase II was practically equal to the same ratio at the miscibility gap border from the \( C_{70} \)-rich side in the \( C_{60}-C_{70} \) system (11,12).

Phase II possibly could be considered as a solvated solid solution of \( C_{60} \) and \( C_{70} \). If that is true, “phase II” with the same \( C_{60}/C_{70} \) ratio could be found in the ternary systems of \( C_{60} \) and \( C_{70} \) with the other solvents. We found such a similar phase in the \( C_{60}-C_{70}-1,2\text{-dichlorobenzene} \) system.

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
solvates $C_{60}S_2C_{70}S_2$ 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 [$\Delta G$ (6) and $\Delta G$ (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:

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

Note: The table and equation are not fully visible in the image provided.
phase diagram of the system C_{60}-C_{70}-1,2-

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

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

*aData from Ref. 13.

at constant temperature and varying X(C_{60}) and X(C_{70}). This means that the activity
coefficients \( \gamma(C_{60}) \) and \( \gamma(C_{70}) \) were equal to those in the binary systems C_{60} and
C_{70} 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 C_{60} and C_{70} in Table 5 were calculated therefore from
the solubilities of C_{60} and C_{70} 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:

\[
RT[0.08 \cdot \ln X_{bin}(C_{70})/X_{ter}(C_{70}) + 0.92 \cdot \ln(X_{bin}(C_{60})/X_{ter}(C_{60})]
= - \Delta G \quad (6)
\]

\[
RT[0.78 \cdot \ln X_{bin}(C_{70})/X_{ter}(C_{70}) + 0.22 \cdot \ln(X_{bin}(C_{60})/X_{ter}(C_{60})]
= - \Delta G \quad (7)
\]

where \( X_{bin} \) and \( X_{ter} \) are solubilities in molar fractions of fullerenes in the binary
and ternary saturated liquid solutions, respectively. Knowing \( \Delta G \) (6), \( \Delta G \) (7),
\( X_{bin}(C_{60}) \), and \( X_{bin}(C_{70}) \), we next calculate \( X_{ter}(C_{60}) \) and \( X_{ter}(C_{70}) \) 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 $X^{290}(C_{60}) = X^{290}(C_{70})$, etc. The solubilities of $C_{60}$ and $C_{70}$, $s(C_{60})$ and $s(C_{70})$, calculated from $X^{290}(C_{60})$ and $X^{290}(C_{70})$, 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 values (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>
<thead>
<tr>
<th>Sample, $C_{60}$/$C_{70}$</th>
<th>Solvent</th>
<th>$s(C_{60})$, mg/mL</th>
<th>$s(C_{70})$, mg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$</td>
<td>1,2-Dimethylbenzene</td>
<td>9.5</td>
<td>-</td>
</tr>
<tr>
<td>$C_{60}$</td>
<td>9.13 mg/ml $C_{70}$ in 1,2-dimethylbenzene</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>5.09:1*</td>
<td>1,2-Dimethylbenzene</td>
<td>15.9</td>
<td>15.6</td>
</tr>
<tr>
<td>1:1</td>
<td>1,2-Dimethylbenzene</td>
<td>13.2</td>
<td>14.9</td>
</tr>
</tbody>
</table>

*"extract": mixture of $C_{60}$ and $C_{70}$ with molar ratio $C_{60}/C_{70}$ 5.09 and admixture of high fullerenes.

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

**CONC**

In this study formation of the 1,2-dimethylbenzene was confirmed. One on the crystal structure of the binary structure (phase II) is different from that of the phase I. The increase of the ideal mixing a reasonable estimation for the stability of the ternary solid phase in equilibrium mixture of phases I and II in the 0.22.

Formation of the binary solvates of $C_{60}$ and $C_{70}$ and salt-in effect was found in the fullerenes in the saturated solutions.

**APP**

The thermodynamic equations for the binary systems $C_{60}$-solvent or $C_{70}$-solvent of phase equilibrium, e.g., for the triangular phase diagram

$$
\mu (\text{phase I}) = x' \cdot \mu (C_{60}) + (1 - x') \cdot \mu (C_{70})
$$

$$
\mu (\text{phase II}) = x'' \cdot \mu (C_{60}) + (1 - x'') \cdot \mu (C_{70})
$$

where $x'$ and $x''$ are fullerenes molar fractions. In our case $x' = 0.92$ and $x'' = 0.08$ to T, $X(C_{60})$, and $X(C_{70})$, one obtains $dX(C_{70})/dT$. Assuming that in the dilute
Equation (9) is no longer valid and has to be rewritten as $x = X^{\text{ter}}(C_{60})$, etc. The solubilities of $C_{60}$ in the liquid solution were determined using the solubility product $k_{sp}$, and the solubility of $C_{60}$ was reached near the melting point of $C_{70}$. The solubility of $C_{60}$ in the liquid solution was found to be $k_{sp}$, and the solubility of $C_{70}$ in the liquid solution was found to be $k_{sp}$.

Measurements were performed to check the accuracy of the solubilities. The measurements were performed at $298 \text{ K}$, and the solubility of $C_{60}$ in the unsaturated solution of $C_{70}$ was found to be $k_{sp}$, and the solubility of the latter solubility were in good accord with the values reported in the literature. However, measurements performed at $308 \text{ K}$, the solubility of $C_{60}$ and $C_{70}$ mixture were found to be $k_{sp}$, and the solubility of the latter solubility were in good accord with the values reported in the literature. In case of $C_{60}$ the solubility of the latter solubility were in good accord with the values reported in the literature.

<table>
<thead>
<tr>
<th>s(C_{60}), mg/mL</th>
<th>s(C_{70}), mg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>10.1</td>
</tr>
<tr>
<td>15.9</td>
<td>15.6</td>
</tr>
<tr>
<td>13.2</td>
<td>14.9</td>
</tr>
</tbody>
</table>

The binary system of $C_{60}$ 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 $C_{60}$, $C_{70}$ 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 $C_{60}S_{2}$. The second crystal structure (phase II) is different from those of the binary solvates of $C_{60}$ or $C_{70}$. Gibbs free energies of the ideal mixing of the binary phases $C_{60}S_{2}$ and $C_{70}S_{2}$ 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 ≤ $x(C_{60})$ ≤ 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 $C_{60}$ to $C_{70}$ in the saturated liquid solutions. Surprisingly, some evidence of the $C_{60}$-$C_{70}$ 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) $X(C_{60})$ and $X(C_{70})$ can be obtained in the same way as for the binary systems $C_{60}$-solvant or $C_{70}$-solvant (7,8). Starting from the conditions of phase equilibrium, e.g., for the triangle I-II-O (Fig. 4),

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

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

where $x'$ and $x''$ are fullerene molar fractions of $C_{60}$ in the equilibrium solid phases. In our case $x' = 0.92$ and $x'' = 0.22$. After differentiation with respect to $T$, $X(C_{60})$, and $X(C_{70})$, one obtains the expressions for both $dX(C_{60})/dT$ and $dX(C_{70})/dT$. 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 \( \mu \) of a solvent is equal to \( \mu \) 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

\[
\frac{d \ln X_{C_{60}}}{dT} = \frac{1}{RT^2} \left\{ \Delta_{\text{sat}} H_{C_{60}} - \frac{(1 - x'') \cdot \Delta_f H_1 - (1 - x') \cdot \Delta_f H_2}{x' - x''} \right\}
\]

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

\[
\frac{d \ln X_{C_{60}}}{dT} = \frac{1}{RT^2} \left\{ \Delta_{\text{sat}} H_{C_{60}} - \frac{(1 - x'') \cdot \Delta_f H_1 - (1 - x') \cdot \Delta_f H_2}{x' - x''} \right\}
\]

where \( \Delta_{\text{sat}} H_{C_{60}} \) and \( \Delta_{\text{sat}} H_{C_{70}} \) are pure fullerenes into the saturated formation of the phases I and II respectively, and \( l = (C_{60})_x (C_{70})_y \) solvates, which are in equilibrium with each other.

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

ACKNOWLEDGEMENTS

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REFERENCES

If X is valid for the solutes, solvent is equal to μ of a pure liquid in the solid solvates is well over the saturated solution, one gets for the compositions

\[ \frac{d \ln X_{C_n}}{dT} = \frac{1}{RT^2} \left\{ \Delta_{s0} H_{C_n} - (x') \cdot \Delta_f H_I - (x'') \cdot \Delta_f H_{II} \right\} \frac{(x' - x'')}{(x' - x'')} \]

where \( \Delta_{s0} H_{C_n} \) and \( \Delta_{s0} H_{C_m} \) 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 = (C_60)_x - (C_70)_x - S_m, and II = (C_60)_x - (C_70)_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 C_{60}-C_{70}-1,2-dimethylbenzene. At the transition temperatures T = 323, 344, or 393 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**


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