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Thermodynamic properties of the binary system C_{60} -1,3,5-trimethylbenzene

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Abstract

Differential scanning calorimetry (DSC), Thermogravimetry (TG) and X-ray showed the formation of two solid solvates of C_{60} with 1,3,5-trimethylbenzene. Temperatures and enthalpies of decomposition of both solvates were measured by DSC. TG and DSC were applied to determine the composition of solvates. The influence of solvates on solubility of C_{60} in 1,3,5-trimethylbenzene was discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimetry; Thermogravimetry; Enthalpies of decomposition; C_{60}

1. Introduction

Following the original method developed by Kratschmer [1], fullerenes are extracted by solvents from soot, and then are separated and purified by liquid chromatography. Crystallisation from the solutions sometimes led to the formation not of a C_{60} , but of solid solvates of C_{60} with the corresponding solvent [2–6]. Formation of solid solvates influences the properties not only of the solid phases. Saturated concentrations in the solution are also dependent on the nature of the equilibrium solid phase. For example, it was shown that the existence of solid solvates is the reason for the unusual temperature dependence of solubility of C_{60} in toluene and *o*-xylene [7–10].

Following our previous investigations of C_{60} -aromatic solvent systems [9,10], now we report the

comprehensive study of the C_{60} -1,3,5-trimethylbenzene system.

2. Experimental

2.1. Materials

Samples of C_{60} were from MER, USA (99.8% mol purity). 1,3,5-trimethylbenzene (FLUKA) was 99% (GC) of purity, boiling temperature = 163–165°C, $n_{D20} = 1.498$.

2.2. Differential scanning calorimetry (DSC)

A DSC-30 Mettler instrument was used to obtain the DSC curves. Standard aluminium pans for Mettler DSC system were employed. A few mg of C_{60} was transferred to the empty pan weighed before and the total weight was determined. Then 1–5 μ l of 1,3,5-

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trimethylbenzene was added from a syringe. The pan was hermetically sealed and weighed again.

Ten samples with different molar ratios of C₆₀ to 1,3,5-trimethylbenzene (from 1:5 to 1:20) have been studied. Each sample was stored at room temperature or in the refrigerator at $T = 260$ K at least for three days before scanning. The scanning rate was 10 K/min. Each pan was scanned several times. The pans were reweighed from time-to-time to check the absence of leakage. The results obtained were independent on the initial molar ratio of C₆₀ to the solvent in the samples.

2.3. Thermogravimetry (TG)

A TG Mettler system was used to obtain TG curves. TG samples were obtained by slow evaporation of saturated solution of C₆₀ in 1,3,5-trimethylbenzene at room temperature. In order to avoid the decomposition of the solvate before starting of the measurements, samples were not specially dried and contained some liquid phase in addition to solid. Five samples (15–30 mg) of C₆₀-1,3,5-trimethylbenzene were heated in the alumina open crucible with the rate of 10 K/min from room temperature up to 620 K under a constant nitrogen flow.

2.4. X-ray measurements

The powder diffractograms of the fullerene solvates were taken at room temperature with the computer controlled DRON 3 powder diffractometer with the graphite monochromator ($\mu\text{Cu K}\alpha = 1.5418 \text{ \AA}$). Unit-cell parameters were determined with the TREOR 90 program.

Samples for the XRD were obtained in the same way as for TG analysis.

3. Results and discussions

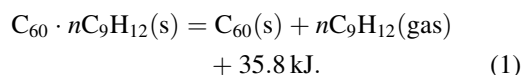
3.1. High temperature solvate (I)

3.1.1. DSC

The first scanning of the samples from 240 K up to the boiling point of 1,3,5-trimethylbenzene did not show any effects. There was no endothermic effect corresponding to the decomposition to the newly

formed solvate as well as the effect of the orientational phase transition in C₆₀, normally observed at 260 K. However, according to our previous experience the absence of the effect at 260 K usually indicates that the reaction between fullerene and the solvent occurred and a solid solvate was formed. In order to clarify the situation two kinds of DSC measurements were additionally performed.

A small hole was made at the top of the pan with C₆₀ and 1,3,5-trimethylbenzene, and then the sample was scanned from 240 up to 620 K, 180° higher than the boiling temperature (T_{bp}) of 1,3,5-trimethylbenzene. Two peaks were presented on the curve (Fig. 1): first wide effect with $T_{\text{max}} \approx T_{\text{bp}}$ of 1,3,5-trimethylbenzene corresponded to the evaporation of the excess of the solvent; the second peak was the endothermic effect, characterised by well reproducible values of $T_{\text{max}} = 460.8 \pm 1.5$ K and $\Delta H = 35.8 \pm 0.5$ kJ/mol of C₆₀. Heating of a pure C₆₀ or of a pure 1,3,5-trimethylbenzene under the same conditions did not show any traces of this second effect, thus confirming that the latter could be explained only by the decomposition of the solvate formed in the system. The corresponding decomposition reaction is



3.1.2. TG

In order to determine the composition of the solvate (n in the Eq. (1)), thermogravimetric analysis (TG) were applied. To confirm the formation of the solvate in the TG samples, one portion of the crystals was heated in DSC from 240 up to 620 K. The presence of the peak at $T = 460.8$ K was detected.

Two well defined steps of decomposition of the samples were observed on the thermogravimetric curve (Fig. 2). First wide step began just at room temperature and was over at 420 K. T_{max} of this step varied from sample to sample depending on the amount of liquid phase present inside the crucible. We considered the weight loss at this step to be due to the evaporation of 1,3,5-trimethylbenzene from the liquid part of the samples. The second step took place in the temperature interval 440–530 K. We considered the weight loss at this step to be due to the decomposition of the solvate (reaction (1)). The results of TG measurements for the second step along with the

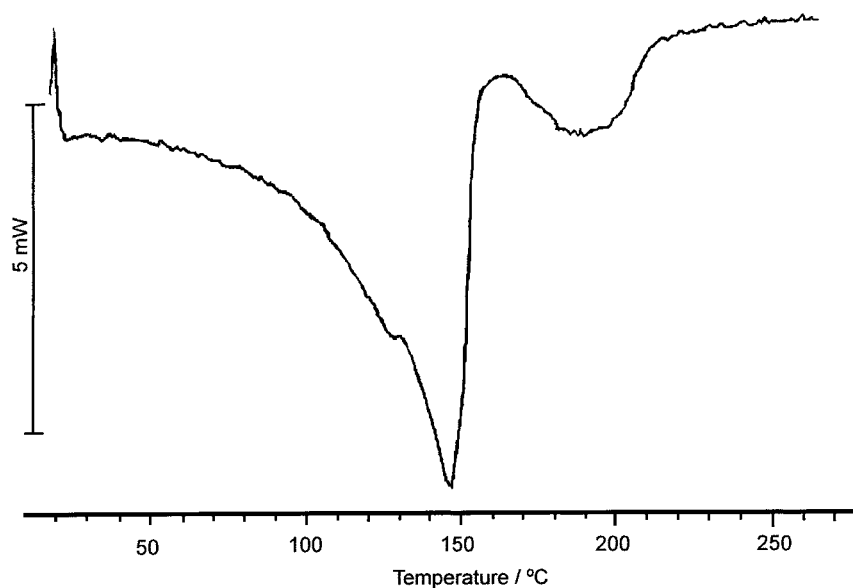


Fig. 1. DSC curve for the C_{60} -1,3,5-trimethylbenzene, pan with the hole (sample mass 8.300 mg, heating rate $10.0^{\circ}\text{C}/\text{min}$).

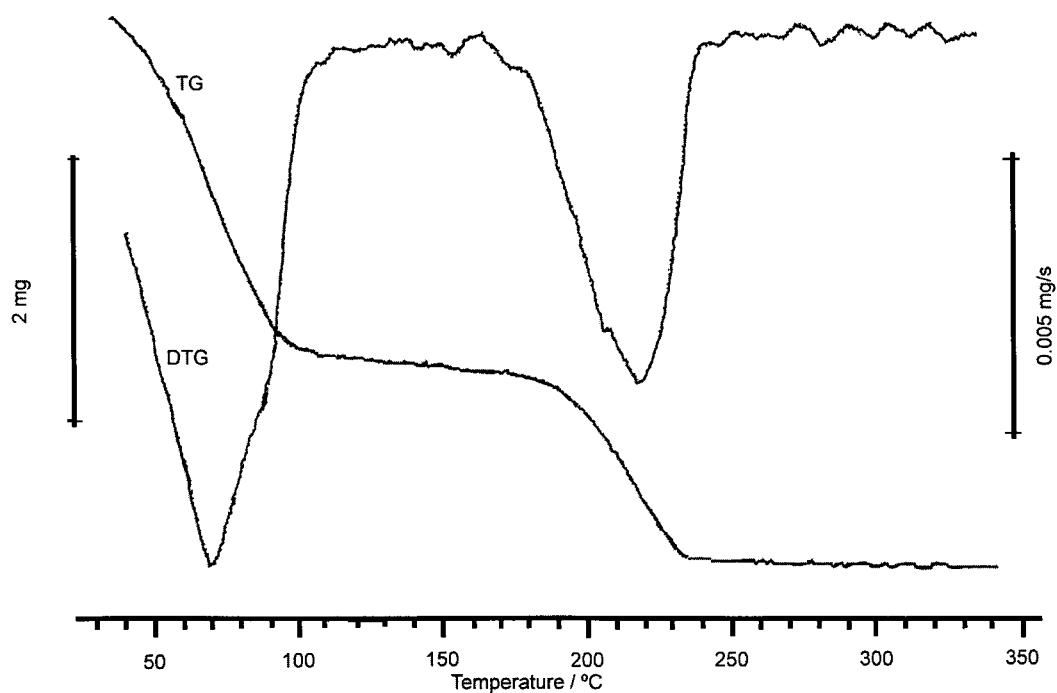


Fig. 2. TG curve of high temperature solvate of C_{60} with 1,3,5-trimethylbenzene (sample mass 20.956 mg, heating rate $10.0^{\circ}\text{C}/\text{min}$).

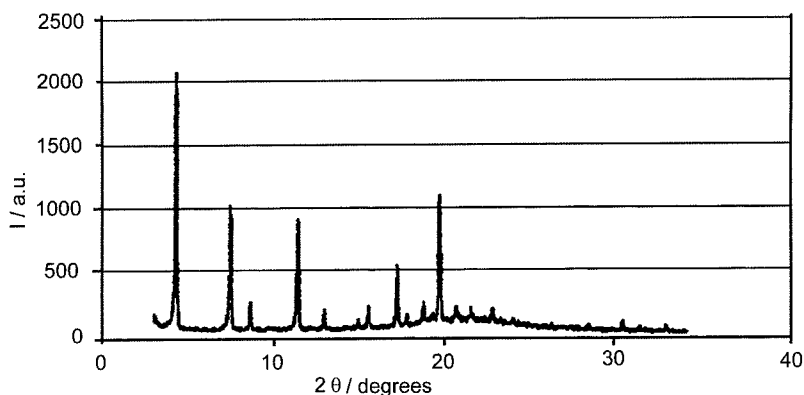


Fig. 3. X-ray powder diffractogram of high temperature solvate of C_{60} with 1,3,5-trimethylbenzene.

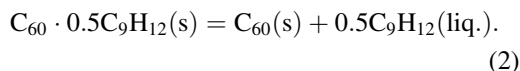
measured weight of the residual solid C_{60} after complete evaporation, allowed one to calculate the composition of the solvate as $C_{60} (0.5 \pm 0.1)C_9H_{12}$.

3.1.3. X-ray measurements

The X-ray powder diffractogram of this solvate is presented in Fig. 3. X-ray data revealed a simple hexagonal unit-cell with parameter values $a = 23.80 \text{ \AA}$, $c = 10.21 \text{ \AA}$ and unit-cell volume = 5010 \AA^3 , ($Z = 6$) was suggested from the calculated density).

3.1.4. Thermodynamic data

The thermodynamic parameters of the reaction (1), combined with the standard enthalpy and the standard entropy of evaporation [11] of the pure solvent, gave the thermodynamic characteristics of the incongruent melting reaction



$\Delta H = 16.3 \text{ kJ/mol}$ and $\Delta S = 33.2 \text{ J/mol/K}$, the hypothetical incongruent melting point at $T = 490 \text{ K}$. The incongruent melting enthalpy per mole of solvent, $\Delta H = 32.6 \text{ kJ/mol}$ is the highest in the series of the solvates of C_{60} with aromatic solvents [9,10]. If we assume that ΔH and ΔS of the reaction (2) are temperature independent, one can calculate ΔG^0 ($T = 298 \text{ K}$) for the reaction (2), the standard Gibbs free energy at $T = 298 \text{ K}$. With the help of this value, the equilibrium vapour pressure of the solvent, $p(S)$, over the mixture of C_{60} with $C_{60} \cdot 0.5C_9H_{12}$ at

$T = 298 \text{ K}$ could be easily found:

$$\begin{aligned} \Delta G^0(298 \text{ K}) &= 0.5RT \ln a(S) \\ &= 0.5RT \ln (p(S))/(p^0(S)), \quad (3) \end{aligned}$$

where $a(S)$ and $p^0(S)$ are, respectively, thermodynamic activity in the solvate and the saturated vapour pressure of $S = 1,3,5$ -trimethylbenzene at room temperature. According to our calculations $\Delta G^0(298 \text{ K}) = 6.4 \text{ kJ/mol}$ and $p(S) = 1.6 \times 10^{-3} \text{ kPa}$. The latter value is 200 times lower than $p^0(S)$. This makes the solvate rather stable: it may be kept in air without a mother liquor for long periods of time.

3.2. Low temperature solvate (II)

Low temperature solvate of C_{60} with 1,3,5-trimethylbenzene was discovered in the following experiment. A hermetically sealed pan containing C_{60} and 1,3,5-trimethylbenzene, after storing for a week at room temperature, was cooled to 200 K and left at this temperature for 1 h. The following scanning up to 420 K showed two endothermic effects: a sharp peak of melting of the solvent at $T_{\max} = 230 \text{ K}$ and a wide unsymmetrical peak beginning at $T = 270 \text{ K}$ with the maximum at $T = 293.8 \text{ K}$ (Fig. 4). Scanning of different samples showed that enthalpy and T_{\max} of this broad peak was highly depended on the conditions in which samples were stored before heating. The longer was the cooling at 200 K , the higher was the enthalpy (up to 44.6 kJ/mol of C_{60}) and T_{\max} (up to 299.2 K). Cooling at higher temperatures

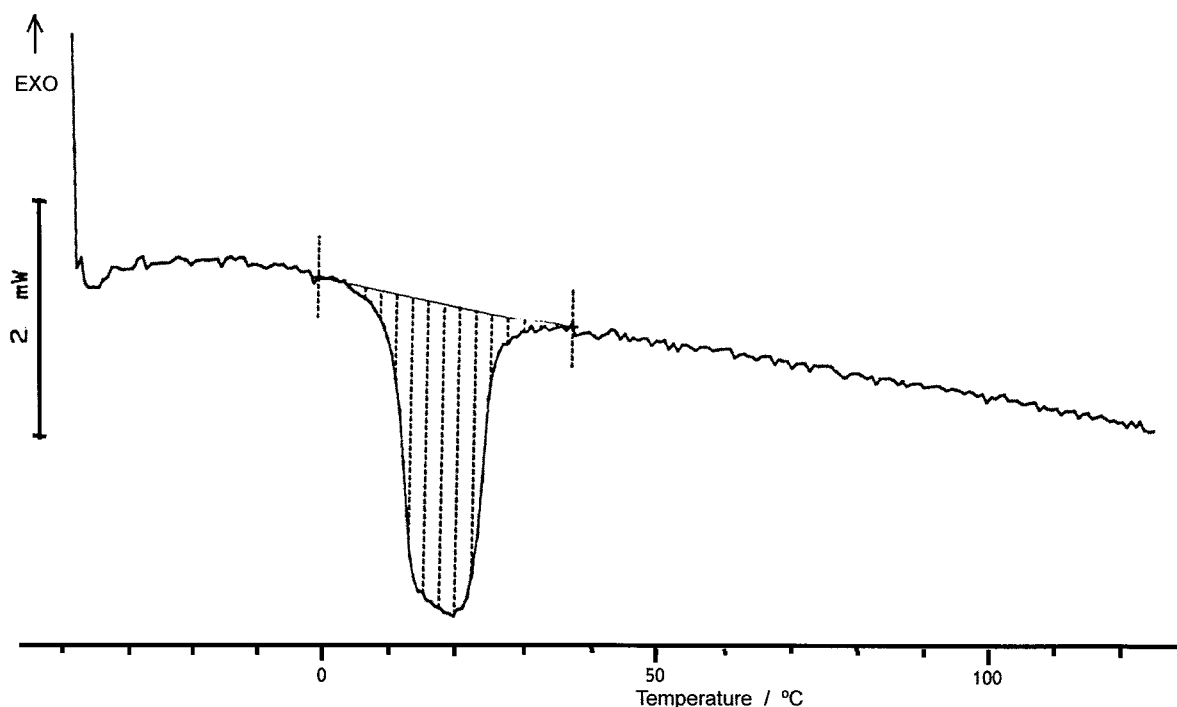


Fig. 4. DSC curve of the C_{60} -1,3,5-trimethylbenzene, hermetically sealed pan. The sample was stored at $T = 200$ K for 1 h (sample mass 7.930 mg, heating rate 10.0 °C/min).

(240–260 K), even for a few days, did not lead to the appearing of this effect on the heating curve.

TG was not applicable to determine the composition of this solvate due to the low temperature of its incongruent melting, DSC offered a method to determine the composition of such solvates. The amount of solvent, which is not incorporated into the solvate was calculated from the area under the peak of melting of the solvent, by comparison with the value of the standard melting enthalpy of 1,3,5-trimethylbenzene. The compositions calculated by this method, changed from measurement to measurement, from 1.8 to 4.1 mol of 1,3,5-trimethylbenzene per mole of C_{60} .

Significant differences in composition and enthalpies of the incongruent melting for different samples could be explained if taking into account that the formation of solid solvates of fullerenes is a slow process, which usually takes from a few hours up to a few months to be completed [7,10]. In our case the reaction starts only if the sample was cooled to the temperature close to the melting point of 1,3,5-tri-

methylbenzene or if the excess of the solvent was frozen. The conditions of our DSC measurements did not offer the opportunity to store the sample at low temperature for more than 3 h, so in some runs this time was not enough for the formation of the solvate to be completed.

The highest values of, ΔH and composition probably corresponded to the complete formation of the solvate (II).

3.3. Comparison with the solubility data

According to the results obtained in the present study, the solid phase in equilibrium with the saturated liquid solution of C_{60} in 1,3,5-trimethylbenzene at room temperature, is a solid solvate rather than pure C_{60} . It is reasonable to assume that this equilibrium solid phase is a high temperature solvate (I) and the solubility of C_{60} in 1,3,5-trimethylbenzene, reported in the literature, is related to it. Present authors gave a simple thermodynamic equation [10] to calculate the

hypothetical solubility, “the solubility, relative to pure C₆₀” at room temperature:

$$\ln(x'/x) = dH/R(1/T - 1/T'), \quad (4)$$

where x' and x are hypothetical solubility (molar fraction) relative to the pure C₆₀ and, experimentally measured solubility, respectively, (molar fraction) relative to the solvate, both at $T = 298$ K, ΔH and “ T' ” are, respectively, the enthalpy of the incongruent melting and the temperature of incongruent melting of the solvate, which is in equilibrium with the saturated solution at $T = 298$ K. According to the Eq. (4), the hypothetical solubility of C₆₀ in 1,3,5-trimethylbenzene, x' , is equal to 0.41×10^{-2} .

Significant and very unexpected difference between the measured solubilities of C₆₀ in 1,3,5- and 1,2,4-trimethylbenzene was reported in the literature [12]. The measured values (molar fractions) were 0.335×10^{-2} and 0.033×10^{-2} at $T = 298$ K for 1,2,4- and 1,3,5-isomers, respectively.

One possible explanation for this could be that these solubilities are determined by solid solvates in equilibrium with the saturated solutions at room temperature, while these solvates in the systems of C₆₀ with 1,2,4- and 1,3,5-trimethylbenzene differ in composition, structure and stability. Positions of CH₃-groups in the guest molecule, different in different isomers, is a governing factor for the formation of the solvates. On the other hand, the interaction of C₆₀ with 1,2,4- and 1,3,5-isomers in the solutions, could be similar.

If the former explanation is true, the hypothetical solubilities x' , rather than measured solubilities x , should be equal for both isomers. Eq. (4) is taking away the influence of solid solvates. The hypothetical solubilities are 1.05×10^{-2} and 0.41×10^{-2} , for 1,2,4- and 1,3,5-trimethylbenzene, respectively. The value for 1,2,4-isomer was obtained, using the data from [4]. It could be stated, that the hypothetical solubilities are more close to each other, compared

to the measured values, though the difference still exists.

Acknowledgements

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