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Thermochimica Acta 299 (1997) 141–144

thermochimica acta

Thermal behaviour of the crystals formed in the Buckminsterfullerene-toluene, o-xylene and bromobenzene systems

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Abstract

Unusual solubility versus temperature dependence for C_{60} fullerene in toluene and several other solvents is due to the formation of solid solvates. Temperature Maximum of Solubility (TMS) in toluene coincides with the incongruent melting point of the solvate with the mole ratio of C_{60} to toluene $1 : 1.8 \pm 0.5$. Similar results were obtained in the system C_{60}–bromobenzene, C_{60}–o-xylene, where solvates with the mole ratio 1 : 2 were found. Stoichiometry of the solvates of C_{60} with the aromatic solvents are discussed in terms of incongruent melting.

Keywords: DSC; Fullerenes; Incongruent melting; Temperature dependence of solubility

1. Introduction

Unusual temperature dependence of the solubility of C_{60} in toluene was first reported by Ruoff et al. [1], and was later confirmed by Xihuang et al. [2]. A negative temperature dependence of solubility along with a temperature maximum of solubility (TMS) around 280 K has been observed. Similar solubility versus temperature curves were found in C_{60}–benzene, C_{60}–hexane [1]. C_{60}–o-xylene [2] systems. For non-aqueous solutions of non-electrolytes, typically with ideal or regular solubility behaviour, such temperature dependence was probably never seen before [1].

In 1995–96, a thermodynamic model was proposed [3,4] to account for the unusual temperature dependence of the solubility of C_{60}. Experimental proofs of this model were first presented in Refs. [5,6].

According to the model maximum of solubility, for example, in the system C_{60}–toluene is due to the formation of a solid solvate (I), which melts incongruently to yield another solvate (II) and liquid saturated solution of C_{60} in toluene. An incongruent melting point could be a temperature maximum of solubility (TMS). At temperatures below TMS a saturated solution is in equilibrium with solvate (I) (k mole of C_{60} per r mole of toluene). Above TMS the saturated solution is equilibrated with solvate (II). In the simplest case solvate (II) may be a pure C_{60}. Phase equilibrium conditions relates x (mole fraction of C_{60} to T (temperature) for both low and high temperature parts of the $T - x$ curve. After certain simplifications, usual for diluted solutions, ($x = 0.0004$ for C_{60} in toluene at $T = 298$ K) one gets:

$$\mathrm{d}\ln x(C_{60})/\mathrm{d}T = \{\Delta H(\mathrm{dis.}, C_{60}) - \Delta H(C_{60}r/kC_7H_8)\}/RT^2 \quad (1)$$

$$\mathrm{d}\ln x(C_{60})/\mathrm{d}T = \Delta H(\mathrm{dis.}, C_{60})/RT^2 \quad (2)$$

for low and high temperature parts of the curve, respectively, is case when the solvate (II) is pure C_{60}.

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PII S0040-6031(97)00170-6

Here $\Delta H(dis., C_{60})$ is an enthalpy of dissolution of C_{60} into a saturated solution and $\Delta H(C_{60}\ r/k\ C_7H_8)$-enthalpy of reaction:

$$C_{60}(s) + r/kC_7H_8(liq) = C_{60}r/kC_7H_8(s) \quad (3)$$

Maximum of solubility is caused by an unusual relation between numbers in the numerators (Eqs. (1) and (2)). The enthalpy of dissolution of C_{60} has to be negative. The enthaply of reaction (3) has to be more negative than the enthalpy of dissolution. The validity of this theory can be proved by the presence in the heterogeneous system C_{60} (s)-solvent of endothermic effect around TMS due to the incongruent melting. The transition should be easily found by DSC. The measured enthalpy of this transition should be equal to the difference of enthalpies calculated from the slopes of the solubility curve above and below TMS.

Here we present some experimental results for the systems C_{60}–toluene, o–xylene, and bromobenzene, which confirm the theory.

2. Experimental

Samples of C_{60} were from MER Ltd. (USA) (99.99% mol purity). Toluene was with the trade mark HP. It was distilled twice before use. Other solvents (o–xylene, bromobenzene) were boiled with sodium in the presence of benzophenon and distilled before use.

A DSC-30 Mettler instrument was used to obtain DSC curves. Measurements were taken at temperatures from 220 K to 350 K with the scanning rates 10 and 5 K/min. Heterogeneous (solid/liquid) samples with different mole ratios of C_{60} to solvent were studied. Before measurement samples were cooled at $T = 268$ K for a period of time from half an hour to one month.

3. Results and discussion

3.1. System C_{60}–toluene

Heterogeneous (solid/liquid) samples with the mole ratio of C_{60} to toluene from 1 : 0.5 to 1 : 80 were studied. Typical DSC curves (increase of temperature) for C_{60}–toluene samples are shown in Fig. 1. For samples prepared just before measurement only peak at 259 K was observed (Fig. 1(a)). For precooled samples two additional endothermic peaks were found (Fig. 1(b)). If samples were cooled for 24 h, the peak of the phase transition at 259 K completely disappeared (Fig. 1(c)). More prolonged cooling did not change the DSC curve. The maximum of the first peak was at 285 ± 1 K, the enthalpy change was 20 ± 2 kJ/mol of C_{60}. For the second broad (probably metastable transition) peak we got $T = 321 \pm 1$ K, and $\Delta H = 10 \pm 2$ kJ/mol. The results of measurements for 12 samples with different compositions were averaged (see Table 1).

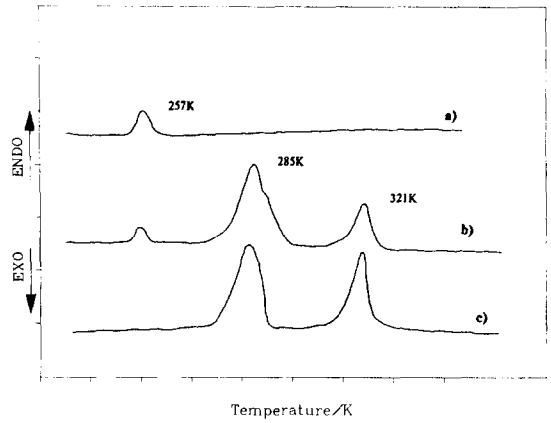

Fig. 1. DSC curves for the C_{60}–toluene samples. (a) the sample was prepared just before measurement; (b) the sample was cooled at 268 K for 2 h before measurement; (c) the sample was cooled at 268 K for 24 h before measurement.

Due to the very low concentration of C_{60} in the saturated solution, the DSC curve (Fig. 1(c)) looked the same way for all samples studied (including one with the composition 1 : 2) except the one with the composition 1 : 0.5. For this composition a peak at 259 K was detectable by DSC even after prolonged cooling. Clearly the ratio r/k in the solvate (I) is at least more than 0.5. When samples were scanned from 350 K to 220 K peaks at 321 K and 285 K disappeared, while the exothermic peak at 259 K reappeared.

Thermodynamic data for the system C_{60}–toluene are summarized in Table 1. The enthalpy difference, calculated from the solubility measurements (differ-

Table 1
Thermodynamics of solubility of C_{60} in toluene, o–xylene, bromobenzene

Thermodynamic function	Method	Enthalpy (kJ/mol)	T/K	Ref.
$\Delta H(diss.,C_{60})-\Delta H(C_{60}*2C_7H_8)$	Solubility	24±2	185–285	[1,6]
$\Delta H(C_{60}*2C_7H_8)$	DSC	−30±3	285	this study
$\Delta H(diss., C_{60})$	solubility	−12±1	285–383	[1,6]
$\Delta H(diss., C_{60})$	calorimetry	−9.2;−5.6;−8.6 (±4)	298	[2,5,4]
$\Delta H(C_{60}*2C_8H_{10})$	DCS	−32±4	320	this study
$\Delta H(C_{60}*2C_6H_5Br)$	DSC	−42±4	350	this study

$\Delta H(C_{60}*2C_8H_{10})$, $\Delta H(C_{60}*2C_6H_5Br)$, $\Delta H(C_{60}*2C_7H_8)$ are the enthalpies of the incongruent melting of the solvates with o–xylene, bromobenzene and toluene, respectively.
$\Delta H(diss., C_{60})$ is the enthalpy of dissolution of C_{60} in toluene.

ence of the slopes of ln x versus $1/T$ dependences above and below TMS) is 36 ± 3 kJ/ mol, in reasonable agreement with the sum of DSC enthalpies at 285 and 321 K. It enables us to consider the decomposition reaction (4)

$$C_{60}2C_7H_8(s) = C_{60}(s) + 2C_7H_8(liq) \quad (4)$$

to be a two-step process at least in the course of DSC measurements. The incongruent melting of (I) at 285 K leads to the formation of the another solvate (II) with less amount of solvent. This latter melts incongruently giving C_{60} and the saturated solution. TMS was observed at 285 K.

3.2. Systems C_{60} o-xylene, bromobenzene

TMS was found in the system C_{60}–o-xylene by the authors [7]. No data on temperature dependence of solubility of C_{60} in bromobenzene were reported.

The results of the DSC study of the heterogeneous mixtures in the systems C_{60}–o-xylene, bromobenzene are presented in Table 1. In both cases two heterogeneous (solid/liquid) samples with the mole ratio of C_{60} to solvent approximately 1 : 5 and 1 : 15 were studied. Endothermic transitions found are incongruent melting points of the solvates in both systems. Entropies of incongruent decomposition (ΔS(reaction 4)) may serve as a basis to classify the solvates. For similar processes the entropies have to be similar. In all three systems studied (o-xylene, bromobenzene, toluene, the sum of two enthalpies, $T = 285$ K) the similar entropies, from 100 to 115 J/mol K were observed. We think (see below) that this entropy corresponds to the decomposition of a solvate with the mole ratio of C_{60} to the solvent 1 : 2.

3.3. Experimental determination of compositions of solvates

DSC scans of the mixtures of solid C_{60} + solvent with the initial composition accurately measured were carried out after the solvates were formed. The compositions used were around 1 : 5. In order to determine the mole ratio of C_{60} to the solvent in the solvates the enthalpy of freezing of the solvent, (which was not therefore included in the solvate) was measured. The ratios 1 : 2.0, 1 : 2.3 were obtained for the solvates with bromobenzene, and o-xylene, respectively.

In the case of toluene the initial mixture with mole ratio 1 : 0.5 was used. For such a mixture the peak of the orientational phase transition did not disappear even after prolonged cooling. The enthalpy of the incongruent melting was lower than usual. In order to determine the stoichiometry of the solvate the ratio of the enthalpy of incongruent melting (samples with the excess of toluene) to the enthalpy of incongruent melting (sample with 1 : 0.5 mole ratio) was measured. On the other hand, the ratio of the enthalpies of the orientational phase transition in pure solid C_{60} and in the 1 : 0.5 C_{60}–toluene sample was determined. Each ratio independently gave the composition of the solvate. The measurements yield the stoichiometry 1 : 1.8 for this solvate. We note that the sample with the initial mole ratio of C_{60} to toluene 1 : 2 showed no presence of the free C_{60}.

The accuracy of all determinations of the composition is (±0.5).

Acknowledgements

This work was supported by the Russian State Program 'Fullerenes and Atomic Clusters' grant 96117. A.L.M. thanks Kodak AO and mutual fund 'Alma Mater Libero' for the financial support.

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