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THERMOCHEMISTRY OF SOLVATED CRYSTALS OF C_{60} AND C_{70} WITH *o*-XYLENE

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Abstract

Differential scanning calorimetry (DSC) was used to study the binary systems of C_{60}–*o*-xylene and C_{70}–*o*-xylene and the ternary system C_{60}–C_{70}–*o*-xylene. Fullerene C_{60} formed solvated crystals $C_{60}\cdot 2C_8H_{10}$ with incongruent melting point 320 K and with enthalpy of decomposition 31±3 kJ (mol of $C_{60})^{-1}$. Two solvated crystals of C_{70} with incongruent melting points 283 and 369 K, and with decomposition enthalpies 18.5±2.2 and 23.0±1.5 kJ (mol of $C_{70})^{-1}$, were formed from *o*-xylene solutions. Three ternary compositions with C_{60}/C_{70} mole ratios of 3:1, 1:1 and 1:3 were scanned by DSC.

Keywords: DSC, fullerenes, solubility, solvated crystals

Introduction

The unusual temperature dependence of the solubility of C_{60} in aromatic solvents was first reported by Ruoff *et al.* [1] and was confirmed by Zhou *et al.* [2, 3]. It was recently shown [4–6] that the solubility behaviour of fullerene C_{60} in aromatic solvents is governed mainly by the formation of solid solvates of C_{60} with the solvent. These solvates change the slope of the temperature dependence of solubility and decrease the absolute values of solubility. Their decomposition even causes solubility maxima. The thermodynamic equations describing this phenomena may be found elsewhere [4–6]. These equations show that the real reason for the appearance of temperature maxima of solubility is the unusual relation between two enthalpies: the enthalpy of formation of the solvated crystal, and the enthalpy of formation of the saturated liquid solution. For fullerenes in aromatics, these two enthalpies have the same negative sign and are comparable.

In the present study, solvated crystals of C_{60} and C_{70} with *o*-xylene were studied with the help of differential scanning calorimetry (DSC).

Experimental

Samples of C_{60} and C_{70} were from MER Ltd. (99.99% mol purity).The solvent had the trade mark HP. It was distilled twice before use.

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A DSC-30 Mettler instrument was used to obtain the DSC curves. Measurements were taken at temperatures from 220 K up to 390 K. The scanning rates were usually 5 or 10 K min^{-1}. The temperatures of incongruent melting were found to depend upon the scanning rates. Extrapolation to zero rate lowered the temperatures of the effects by 5–10 K. These extrapolated values were believed to correspond to the real temperatures of equilibrium transitions. The same conclusion was made by the authors [7]. The temperatures of the maxima of the DSC peaks are presented. The exo- or endothermic heats of transitions proved to be independent of the scanning rate.

Heterogeneous (solid/liquid) samples with different mole ratios of C_{60} to C_{70} and to the solvent were studied. The mole ratio of solvent to fullerenes was less than 10 for all samples. With such a ratio, more than 98 per cent of the fullerenes was kept in the solid phase rather than in the saturated liquid solution.

Each sample was scanned several times. Before each measurement, samples were left to stand at room temperature or at 268 K in the refrigerator for a period of time ranging from half an hour up to one month. Data on the samples with different pre-histories were compared in order to prove that the equilibrium phase composition was reached in the course of the measurements. Further details of the experimental procedure were described elsewhere [2, 4].

In order to determine the compositions of co-solvates, DSC scans of the mixtures of solid C_{60}+solvent or C_{70}+solvent with the initial compositions accurately measured were carried out after the co-solvates were formed. The compositions used were around 1:5. The enthalpies of freezing and melting of the free solvent, which had not reacted with the fullerenes, were measured.

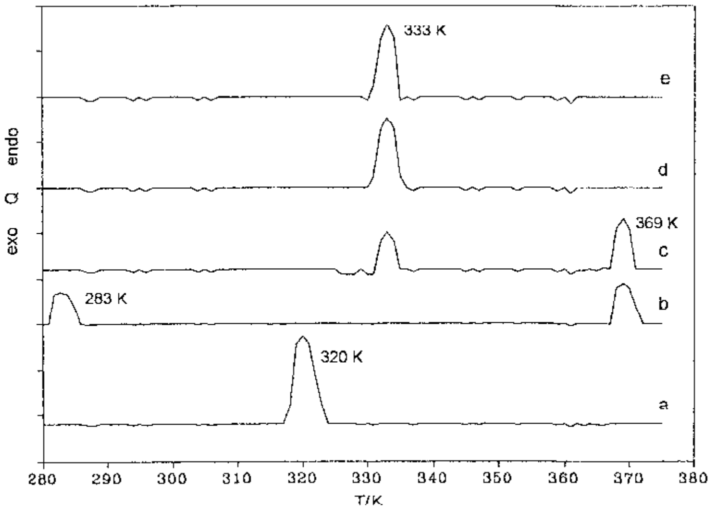

Fig. 1 DSC curves. a) C_{60}–*o*-xylene; b) C_{70}–*o*-xylene; c) ternary system, A; d) ternary system, B; e) ternary system, C

Results and discussion

System C_{60}–o-xylene

In the present study, five heterogeneous (solid/liquid) samples with mole ratios of C_{60} to *o*-xylene of from 1:0.5 up 1:10 were examined. A typical DSC curve (upscan) is given in Fig. 1a. It shows an endothermic peak at 320±2 K and no peak of the orientational phase transition in C_{60}. The mean value of the measured enthalpy was 31±3 kJ mol^{-1} of C_{60}. This enthalpy was attributed to the incongruent decomposition of a solvate of C_{60} with *o*-xylene with mole ratio 1:2.

$$C_{60}\cdot 2C_8H_{10}(s) = C_{60}(s) + 2C_8H_{10}(liq) \qquad (1)$$

The Gibbs energy of reaction (1) at 298 K, calculated from the enthalpy and the temperature of this transition (see above), is equal to 2.3 kJ mol^{-1}. This means that at 298 K the partial pressure of *o*-xylene over a solid mixture of C_{60} with $C_{60}\cdot 2C_8H_{10}$ is 1.5 times lower than the saturated vapour pressure of pure liquid *o*-xylene. On the other hand, formation of a co-solvate lowers the solubility of C_{60} in *o*-xylene by a factor of 2.4.

Solubility measurements [2, 3] confirmed the existence of the temperature maximum of solubility, though at slightly lower temperature (303–313 K). Extrapolation of the DSC data to zero scanning rate makes the disagreement in temperatures smaller. Figure 2 presents ln*x* *vs.* 1/*T* for this system (*x* and *T* are the mole fraction of C_{60} in the saturated solution and the temperature in K, respec-

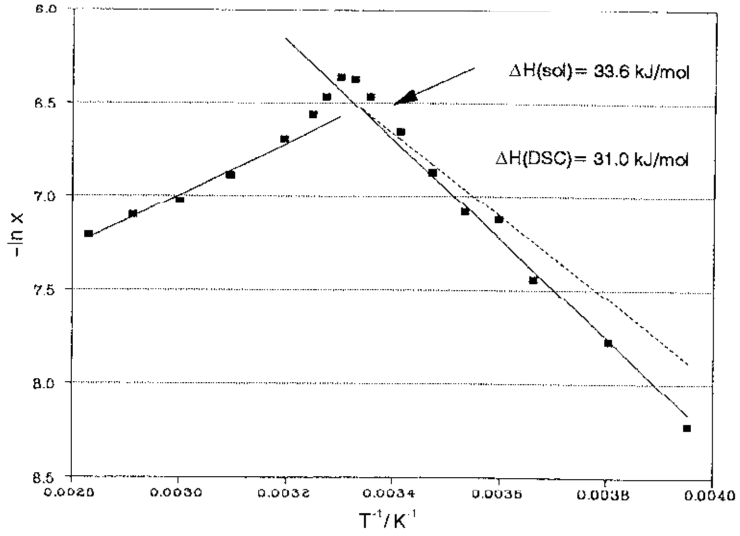

Fig. 2 Temperature dependence of solubility of C_{60} in *o*-xylene. Filled squares – Ref. [3]; dashed line – the slope calculated from the DSC data

tively. The difference in the slopes above and below the maximum should be equal to the enthalpy of incongruent decomposition of the solid solvate (Eq. 1). The agreement between the two numbers is good.

System C_{70}–o-xylene

Three samples of C_{70} with *o*-xylene were scanned by DSC. A typical upscan is presented in Fig. 1b. It shows two incongruent melting transitions at 283.0±1.8 K and 368.7±1.2 K, with enthalpies of 18.5±2.2 and 23.0±1.5 kJ (mol of C_{70})$^{-1}$, respectively. Two solid solvates with different mole ratios of C_{70} to *o*-xylene were formed in the system. With the DSC procedure described above, the composition of the high-temperature solvate was determined as 1:2 (C_{70}/*o*-xylene). This solvate was isolated by drying under air at room temperature. A DSC upscan of the dry sample showed an endothermic peak at 369 K with ΔH equal to 22.3 kJ (mol of C_{70})$^{-1}$. The low-temperature solvate incorporates at least one additional mole of solvent C_{70}/*o*-xylene = 1:3 or 1:4).

The DSC results presented do not fit the data on solubility and on the enthalpy of dissolution [2, 3] of C_{70} in *o*-xylene (Fig. 3). In the early paper by Zhou *et al.* [2], the solubility curve showed no evidence of the incongruent decomposition at 283 K. Such evidence could be found though in the more recent paper from the same authors [3]. The decomposition temperature of the second solvate (369 K) was above the temperature interval of the solubility measurements. The positive enthalpy of dissolution, 3.73±0.02 kJ mol^{-1} [3], combined with the enthalpy of de-composition at 369 K, should give a positive slope of the temperature depen-dence

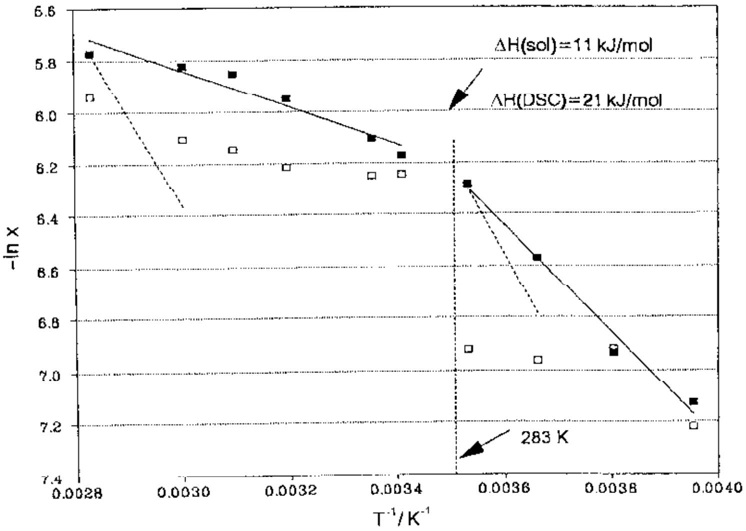

Fig. 3 Temperature dependence of solubility of C_{70} in *o*-xylene. Empty squares – Ref. [2]; filled squares – Ref. [3]; dashed line – the slopes calculated from the DSC data

of solubility (ln$x$ *vs.* 1/T), with the corresponding ΔH equal to 27 kJ mol^{-1} at temperatures between 283 and 369 K, and a very positive slope (ΔH=45 kJ mol^{-1}) below 283 K. The experimental slopes are much smaller (Fig. 3). It is difficult to say whether or not a maximum of solubility exists at 369 K.

It could be speculated that equilibrium conditions were not reached in the course of solubility measurements, at least at low temperatures, and/or that the results on the enthalpy of dissolution of C_{70} in *o*-xylene were erroneous. The DSC data from this study are also open to criticism. It should be mentioned, however, that our enthalpies of incongruent melting could be underestimated, rather than overestimated, due to the lack of equilibrium (incomplete conversion of C_{70} into solvates). Higher enthalpies of decomposition at 283 K and 369 K will make the disagreement with the solubility data even worse.

Ternary system

Three ternary compositions, with mole ratios of C_{70} to C_{60} of 3:1 (A), 1:1 (B) and 1:3 (C), were studied. First, three samples with the compositions A, B and C were simply sealed in the DSC pans. Next, two samples with the compositions B and C were carefully ground before DSC scans. In all samples, the excess of the solvent guaranteed the presence of a liquid saturated solution in the final equilibrium mixture. This saturated solution was a very dilute one, practically with the properties of pure liquid *o*-xylene. The samples were left to stand at room temperature or in the refrigerator for a period of time from 2 days up to 2 weeks prior to the DSC study. Up scanning from 290 K to 393 K was performed for all samples. Each sample was scanned several times, being left at room temperature or in the refrigerator for 5–7 days between the runs. No significant dependence of the DSC results on the pre-history of the samples was found. The only controlling factor was the initial mole ratio of C_{60} to C_{70} in the sample.

Typical DSC curves for samples A, B and C are presented in Fig. 1c, d and e, respectively. The following features of the curves should be emphasized:

- Neither of the curves resembles the superposition of the curves for binary samples.
- The new effect was observed at the same temperature of 333±2 K for all of the samples studied. This effect could be explained by the incongruent melting of a ternary solvate of C_{60} with C_{70} and *o*-xylene.
- The effect at 369 K was observed only for sample A, enriched with C_{70}. This effect could be explained by the incongruent melting of the binary solvate $C_{70}\cdot 2C_8H_{10}$.
- For all the samples studied, the total endothermic heat measured was significantly lower than could be expected; it seemed that less than 2 moles of *o*-xylene per mole of fullerene C_{60} and/or C_{70} was incorporated in the ternary solid phase, or another ternary phases existed in the system.

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