Calorimetric Studies of Solvates of C$_{60}$ and C$_{70}$ with Aromatic Solvents

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To improve the understanding of the solution properties of C$_{60}$ and C$_{70}$ in aromatic solvents, binary systems of C$_{60}$ and C$_{70}$ with benzene, toluene, 1,2- and 1,3-dimethylbenzene, 1,2,4- and 1,3,5-trimethylbenzene, bromobenzene, and 1,2- and 1,3-dichlorobenzene were studied using differential scanning calorimetry, solution calorimetry, and thermogravimetry. Solid solvates with different compositions were identified in many of the systems. The solvates were characterized by composition and by the temperature and the enthalpy of the incongruent melting transition. Enthalpies of solution of C$_{60}$ in toluene, 1,2-dimethylbenzene, 1,2- and 1,3-dichlorobenzene, and 1,2,4-trimethylbenzene and of C$_{70}$ in 1,2-dimethylbenzene and in 1,2- and 1,3-dichlorobenzene were determined. The formation–incongruent melting of solid solvates causes maxima in the temperature–solubility curves of fullerenes in aromatic solvents. Trends in solubility behavior of fullerenes were discussed in terms of thermodynamics of solution and solvate formation.

Introduction

The unusual temperature dependence of solubility of fullerenes in a number of solvents[1] has attracted attention and provoked experimental studies in different laboratories. Until now temperature maxima of solubility were observed in the two-component systems of C$_{60}$ with toluene and CS$_2$[1,2] and with 1,2-dimethylbenzene,[2] 1,2-dichlorobenzene, tetralin, and 1,3-diphenylacetone.[3] Similar effects have been observed in systems with C$_{70}$ and 1,2-dichlorobenzene, tetralin, and 1,3-diphenylacetone.[3] The solubility maxima were shown to arise from the existence of solid solvates formed by the fullerenes with the solvent[4–7] and from their decomposition (incongruent melting).

Another intriguing feature of the solution behavior of the fullerenes is the large difference in solubility at ambient temperature observed for positional isomers such as 1,2- and 1,3-dichlorobenzene (25 and 2.4 mg/mL of C$_{60}$, respectively)[8] and 1,2,4- and 1,3,5-trimethylbenzene (18 and 1.5 mg/mL of C$_{60}$).[9] The chemical properties in the liquid phase of the two pairs of solvents are similar.

The maximum of solubility in the system C$_{60}$–B is due to the formation of a solid solvate (**I**), which melts incongruently to yield pure C$_{60}$ in the presence of liquid solvent B saturated with C$_{60}$. The incongruent melting point is the temperature of maximum solubility, T_{max}. At temperatures below T_{max} a saturated solution is in equilibrium with the solvate (**I**) (n moles of B per mole of C$_{60}$, where n is an integer or a rational fraction). Above T_{max} the saturated solution is equilibrated with another

solvate (**II**), or more probably, pure C$_{60}$. Phase equilibrium conditions relate the mole fraction of C$_{60}$, $x(C_{60})$, to T (temperature) for both low- and high-temperature parts of the $(\ln x)$–T curve. After certain simplifications, usual for dilute solutions, one gets

$$\mathrm{d}\ln x(\mathrm{C}_{60})/\mathrm{d}T = \frac{\Delta_{sol}H^{\circ} + \Delta_r H}{RT^2} \tag{1}$$

$$\mathrm{d}\ln x(\mathrm{C}_{60})/\mathrm{d}T = \frac{\Delta_{sol}H}{RT^2} \tag{2}$$

for low- and high-temperature parts of the curve, respectively, when the solvate (**II**) is pure C$_{60}$. Here, $\Delta_{sol}H$ is the enthalpy of solution of C$_{60}$ and $\Delta_r H$ is the enthalpy of reaction of incongruent melting of solvate C$_{60}\cdot n$B:

$$\mathrm{C}_{60}\cdot n\mathrm{B(s)} = \mathrm{C}_{60}(\mathrm{s}) + n\mathrm{B(liq)} \tag{3}$$
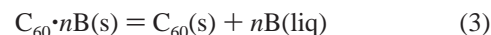
In order for a maximum of solubility to occur, the incongruent melting has to take place below the normal boiling point of the solvent and the enthalpy of solution of C$_{60}$ must be negative but the sum of the enthalpies in eq 1 must be positive. These equations are strictly thermodynamic; i.e., the possible role of kinetic factors is ignored.

In this work a systematic study of the binary systems of C$_{60}$ and C$_{70}$ with various aromatic solvents was performed. Differential scanning calorimetry (DSC) and thermogravimetry

(TG) were used in order to search for new solid solvates with incongruent melting points. When solid solvates were found, they were characterized by their temperatures and enthalpies of the incongruent melting and by composition. Solution calorimetry supplied information about enthalpies of pure and solvated fullerenes in the solvents. When possible, results were compared with existing solubility data in order to show the applicability of eqs 1 and 2. Trends in solvate stability were examined. Finally, the thermodynamic data were combined in order to discuss absolute values of solubility of C_{60} and C_{70} in aromatic solvents.

Experimental Section

Materials. C_{60} from MER Corp., Tucson, AZ (99.9%), was doubly sublimed. In Lund, samples of two different batches (A and B) of C_{60} were gently ground in an agate mortar. After being ground, sample A was left to stand overnight in air at 100 °C before use. Sample B was sieved and the fraction separated; between 100 and 150 mesh sieves were used. A doubly sublimed sample of C_{70} (MER Corp., >99%) was used after gentle grinding in an agate mortar. The same fullerene samples were used in Moscow without any preliminary treatment.

Aromatic solvents, purchased from different companies, had stated purities in all cases better than 98%. ^{1}H NMR and IR spectra were used to confirm the identity and purity of the solvents. The melting points measured with DSC for all the solvents were close (±0.2 °C) to the known literature values. Most solvents were used without further treatment, but some were distilled before use. The additional distillation did not influence the final calorimetric results.

DSC Measurements. The instruments used were DSC-30 Mettler (Moscow) and Perkin-Elmer DSC-2 (Lund). Measurements were taken at temperatures from 200 K up to 390 K. The scanning rates were usually 10 or 5 K/min in Moscow and 2.5 K/min in Lund. Additional runs were performed on the system C_{60}-toluene with the scanning rates 20, 2.5, 2, and 1 K/min. Heterogeneous (solid–liquid) samples with different mole ratios of C_{60} and C_{70} to the solvent were studied. Mole ratios of solvent to fullerenes were less than 15 in most of the samples. With such ratios more than 98% of fullerenes were kept in the solid phase rather than in the saturated liquid solution. Each sample was scanned several times. Before each DSC run samples were left to stand at room temperature or at 268 K in a refrigerator for a period of time from half an hour up to several months. Typically, three to five samples of different compositions and prehistory were studied in each system. Data for different samples were collected and compared in order to prove that the equilibrium phase composition was reached in the course of measurements.

DSC offered a method to determine the composition of the solvate $C_x \cdot n$B ($x = 60$ or 70) by determining the amounts of C_x and B in the sample that had not reacted to form solvate. The amount of excess solvent was determined from the size of the solvent melting peak in DSC experiments by comparing the excess solvent peak with the peak recorded for a known amount of pure solvent. The extent of reaction of C_{60} in the sample could be followed through the order–disorder transition of C_{60} around 260 K. Solvate composition was determined only for samples where this peak had completely disappeared, indicating complete conversion of C_{60} to solvate. The samples containing C_{70} were treated in the same way. The C_{60}-toluene system could not be studied in this way because of the low melting point of toluene. Further details of the experimental procedure have been described elsewhere.[4,6,7]

TG Measurements. TG measurements were performed in Moscow with the Mettler thermobalance in order to determine the compositions of the solid solvates. Solvates were precipitated from the saturated solution, the liquid phase was removed, and the solid sample was carefully dried just before measurements. In a typical TG measurement the amount of solvent that evaporated as the sample was heated to 450 K was determined. Three to five samples of each solvate were examined. With all precautions taken, there was still a danger that some of the solvent was lost before the TG run during the preparation of the solvate (see below).

Solution Calorimetry. The enthalpies of solution $\Delta_{sol}H$ of C_{60} and C_{70} were measured by direct calorimetry. $\Delta_{sol}H$ of C_{60} in 1,2-dimethylbenzene at 298 and 323 K were measured using the 2225 Precision Solution calorimeter (Thermometric, Järfälla, Sweden). It is a semiadiabatic macrocalorimeter with a 100 mL glass reaction vessel. Glass sample ampules of cylindrical shape and with thin end walls were charged with 50–60 mg of C_{60} and the thin-walled necks sealed under low flame. The measured enthalpy changes were corrected for a small endothermic background effect observed when breaking empty ampules in the filled calorimetric vessel. The effect is mainly due to the introduction of a small air bubble (∼1 mL) into the calorimeter liquid, which results in evaporation.

The macrosolution calorimeter requires fairly large samples, so to reduce the consumption of the fullerenes, we have used for most of the experiments a microcalorimeter that was recently developed for the determination of enthalpies of solution of solid samples.[10] It is an isothermal, twin heat conduction calorimeter in which the solution vessel of 20 cm^3 volume can be removed from the measurement position for cleaning and charging. A massive ampule made of stainless steel is used as a passive reference. The calorimeter proper is of the same design as calorimeter E in Bäckman et al.[11] and has the same properties as described in the reference. The calorimeter is used in the high-precision thermostatic water bath of the 2277 TAM thermal activity monitor system (Thermometric AB, Järfälla, Sweden). We also used their amplifier and data acquisition system. The insertion vessel, made of high-grade stainless steel, is fitted with a stirrer and four devices for the injection of samples. The density of the fullerenes is usually much higher than that of the solvents, and the solubility is limited so that efficient stirring is needed to ensure complete and reasonably fast dissolution. We have used a turbine stirrer made of stainless steel in combination with a gold propeller and a stirring speed of about 100 rpm. The fullerenes react with the solvents studied to form solid solvates, so the samples must be protected from solvent vapors during the equilibration period. Small collapsible ampules with an interior volume of 40 mm^3, which were mounted in hermetically sealed compartments in the lid of the vessel, were used. To initiate the solution process, the ampule is pushed down so that it falls apart in the solution and exposes the sample to the solvent. There are four sample compartments in the lid, allowing up to four consecutive experiments to be made in the same filling of the calorimeter vessel. The introduction of the ampule is accompanied by a small heat effect that was determined from separate experiments injecting empty ampules into the solvent.

Results and Discussion

DSC and TG Results. DSC measurements showed the formation of solid solvates of C_{60} and C_{70} with the solvents in a number of systems studied. The formation of solvates was detected by the appearance of large peaks (18–45 kJ mol^{-1} of

TABLE 1: Thermodynamics of Solid Solvates of C_{60} and C_{70} with Aromatic Solvents Determined from DSC Experiments

fullerene−solvent	solvate composition (C_n/solvent)	T_{imp}, K	$\Delta_r H$, kJ/(mol C_x)	$\Delta_r S$, J/(K mol C_x)
C_{60}−benzene	1:(3.8 ± 0.2)	322 ± 1[a]	41 ± 1	127
	(1:4)[c]			
C_{60}−toluene	1:(1.8 ± 0.2)	285.0 ± 0.2[a]	19 ± 1	105
		285 ± 1[b]	20 ± 2	
		331 ± 1[b]	10 ± 2	
C_{60}−1,2-dimethylbenzene	1:(2.0−3.4)	318[a]	30 ± 2	94
	1:(2.1 ± 0.2)	322.0 ± 2.6[b]	31.3 ± 1.4	97
C_{60}−1,3-dimethylbenzene	1:(2.3−3.6)	294.0 ± 1.0[b]	24.3 ± 3.0	83
		332.0 ± 1.2[b]	3.2 ± 0.3	9
		370.0 ± 3.7[b]	11.9 ± 0.7	32
C_{60}−1,2-dichlorobenzene	1:(2.0−2.7)	322[a,d]	18.5 ± 2.3	57
	1:(2.0 ± 0.5)	342[a,b,e]	18.9 ± 1.5	55
C_{60}−1,3-dichlorobenzene	1:(2.3 ± 0.5)	308.5 ± 1.3[a]	28.5 ± 1.2	92
		406 ± 3[a]	12.2 ± 0.9	30
C_{60}−1,3,5-trimethylbenzene	1:(2.0−4.0)	292−300[b]	25−44	146
	1:(0.5 ± 0.2)	296[a]	28 ± 3	95
		460.8 ± 1.5[b]	16.3 ± 0.6	33
C_{60}−1,2,4 trimethylbenzene	1:(1.7−2.4)	322[a]	38.2 ± 0.4	119
C_{60}−bromobenzene	1:(2.0 ± 0.2)	350 ± 1[b]	42 ± 2	121
	(1:2)[f]			
C_{70}−1,2-dimethylbenzene	1:(3.0−4.0)	283.0 ± 1.2[b]	18.5 ± 1.5	57
	1:(2.0 ± 0.5)	368.7 ± 0.8 [b]	23.0 ± 1.0	63
C_{70}−1,2-dichlorobenzene	327.9 ± 1.1[a]	8.7 ± 0.9	24	
		397.5 ± 1.0[a]	21.4 ± 1.1	48
C_{70}−bromobenzene	1:(1.9 ± 0.2)	290 ± 1.0[b]	16.2 ± 1.2	56

[a] Measured in Lund. [b] Measured in Moscow; footnotes a and b refer to the whole line in the Table. [c] From refs 17 and 18. [d] Freshly prepared sample. [e] After storage. [f] From ref 7. T_{imp} is the incongruent melting point of the solvate.

fullerene) arising from the incongruent melting transitions, reaction 3, and by the disappearance of the smaller peaks (5−8 kJ mol⁻¹) from the solid−solid phase transitions in the pure fullerenes. These latter peaks reappeared again after the solid solvates were destroyed by incongruent melting.[4,6] The results are summarized in Table 1. The first column gives the system and the second the composition of the solvates formed. The melting−decomposition temperatures T_{imp}, defined as the maximum temperature of the peaks, are shown in the third column. The enthalpies of decomposition of the solvates, $\Delta_r H$, determined from the (endothermic) DSC peaks are given in the fourth column and the corresponding entropy changes $\Delta_r S$ in the last column. In some of the systems more than one solvate was identified. In all cases except one (system C_{60}−1,3,5-trimethylbenzene, peak at 460.8 K) the incongruent melting transitions took place below the normal boiling point of the solvents. No new peaks were observed below the normal boiling points of the solvents in the systems of C_{70} with benzene, toluene, 1,3,5-trimethylbenzene, 1,3-dimethylbenzene, and 1,3-dichlorobenzene.

All of the solvates studied were relatively stable van der Waals complexes with enthalpies of reaction of 10−35 kJ (mol solvent)⁻¹. These are larger than the reaction enthalpies of the solvates of C_{60} with some alkanes and cycloalkanes[12−15] and the complex $C_{70} \cdot C_7 H_8$,[16] which are about 3−8 kJ (mol solvent)⁻¹. The entropy changes are also larger for the decomposition of the complexes with the aromatic solvents in our study compared to the solvates of the saturated hydrocarbons.[12−16]

Some of the solvates (such as C_{60}−1,2-dimethylbenzene, C_{60}−bromobenzene, C_{60}−1,2-dichlorobenzene, and C_{70}−1,2-dimethylbenzene) gave well-shaped peaks with reproducible temperatures and enthalpies of the incongruent melting. The composition of these solvates was easily determined. In some other cases ("low-temperature solvates" in the systems C_{60}−1,3-dimethylbenzene and C_{60}−1,3,5-trimethylbenzene) peaks arising from the incongruent melting transition were broad and had irregular shape. Furthermore, the temperature and the

enthalpy of the transition as well as the composition of the solvate varied from sample to sample. As a rule, higher enthalpies corresponded to a higher transition temperature. It can be assumed that solubility measurements where the solid phase consists of such solvates will be difficult to reproduce because of the slow kinetics of their formation and dissolution.

The composition of the solvate C_{60}−1,2-dimethylbenzene and the "high-temperature solvate" in the system C_{70}−1,2-dimethylbenzene was determined from routine TG measurements, which gave loss of weight of the solvate corresponding to the complete evaporation of the solvent. These solvates were prepared by precipitation from saturated solutions, and the TG results showed that they had the same stoichiometry as the solvates formed in the reaction of the solvent with the solid fullerenes. The vapor pressure of solvent over the solvate may be high enough to cause weight losses,[7] which makes measurements of their composition by TG less accurate.

Some of the solvates shown in Table 1 had a composition close to 1 mol of C_x to 2 mol of solvent (x = 60, 70). On the basis of the X-ray structure obtained for the solvate $C_{60} \cdot 2 C_6 H_5$-Br,[7] the composition of all these solvates was considered to be exactly 1:2, though experimentally measured numbers were slightly different (see Table 1). For similar reasons, the composition of the solvate of C_{60} with benzene was taken to be 1:4 as stated by the authors of the X-ray studies.[17,18] In all other cases Table 1 gives only the experimentally determined compositions.

Solution Enthalpies. The results of the microcalorimetric experiments to determine enthalpies of solution at 298 K of C_{60} and C_{70} in various organic solvents are summarized in Table 2. The found values of the enthalpies of solution are shown in the second column where the uncertainties are expressed as the estimated standard deviation of the mean based on four to six experiments. Between 1 and 6 mg of fullerene was dissolved in 18−9 mL of solvent with two or three consecutive measurements in each filling, giving final concentrations between 0.1

TABLE 2: Enthalpies of Solution of C_{60} and C_{70} in Some Aromatic Solvents Determined from Microsolution Calorimetric Experiments at 298 K

fullerene−solvent	$\Delta_{sol}H$, kJ/(mol C_x)	$\Delta_{sol}H$, kJ/(mol C_x) [ref]
C_{60}−toluene		−8.6 ± 0.7 [5]
		−8.3 ± 0.7 [6]
		−7.54 ± 0.02 [21]
C_{60}−1,2-dimethylbenzene	−14.53 ± 0.30	−10.8 ± 0.1 [21]
C_{60}−1,2,4-trimethylbenzene	−17.72 ± 0.40	
C_{60}−1,2-dichlorobenzene	−13.72 ± 0.15[a]	
	−14.22 ± 0.20[b]	
C_{60}−1,3-dichlorobenzene	−12.49 ± 0.18	
C_{60}−bromobenzene		−11.5 ± 2.0 [7]
C_{70}−toluene	−15.21 ± 0.70	+1.38 ± 0.34 [21]
C_{70}−1,2-dimethylbenzene	−18.84 ± 0.62	+1.93 ± 0.03 [21]
C_{70}−1,2-dichlorobenzene	−18.67 ± 0.34	
C_{70}−1,3-dichlorobenzene	−17.60 ± 0.36	

[a] Sample A. [b] Sample B.

and 0.6 mmol/L in the final solution. Solute−solute interactions can be expected to be negligible at these low concentrations.[19]

The introduction of the ampule is accompanied by a small heat effect that was determined from separate experiments injecting empty ampules into the solvent. The correction for C_{60} in the first two solvents and the first series of 1,2-dichlorobenzene was significantly exothermic, −7.37 ± 0.46 mJ (11 experiments), indicating sizable friction. The injection mechanism was adjusted, and thereafter, the correction was 2.21 ± 0.23 mJ for the second series of C_{60} in 1,2-dichlorobenzene and for C_{70} in 1,2-dimethylbenzene. For the experiments with toluene the observed effect was 7.31 ± 1.01 mJ of which 2.5 mJ can be ascribed to the heat effect arising from saturation of the 40 mm³ air bubble introduced by opening of the ampule. Only toluene has enough high vapor pressure to give a significant evaporation effect. For the remaining series, the correction was zero. Two different samples of C_{60} were used for measurements in 1,2-dichlorobenzene, but as seen from Table 2, the difference between the observed $\Delta_{sol}H$ is not significant. We can conclude that the batch-to-batch variation and the somewhat different sample treatment did not have any observable effect on the dissolution enthalpy.

The enthalpy of solution $\Delta_{sol}H$ of C_{60} in 1,2-dimethylbenzene was determined at 298.15 and 323.15 K using the macrosolution calorimeter. The C_{60} sample A from the second grinding was used. The dissolution was fast at both temperatures, and reaction periods of about 15 min were used when evaluating the calorimetric experiments. The following results were obtained: $\Delta_{sol}H = (−14.37 ± 0.40)$ kJ/mol at 298.15 K and $(−12.08 ± 0.16)$ kJ/mol at 323.15 K on the basis of three dissolution experiments at each temperature. The value at 298 K is in excellent agreement with the value determined from the microcalorimetric experiments (see Table 2).

The values of $\Delta_{sol}H$ for the dissolution of C_{60} in 1,2-dimethylbenzene at the two temperatures gives 95 ± 15 J/K mol for the heat capacity change $\Delta C_{p,sol}$ for the dissolution process. $\Delta C_{p,sol}$ is the heat capacity of C_{60} in solution minus the heat capacity of crystalline C_{60}. Considering the change of state of aggregation for C_{60}, the increase in heat capacity upon dissolution appears fairly modest. The heat capacity of solid C_{60} at 298 K is 536.9 J/K mol.[20]

Values of solution enthalpies reported in the literature are shown in the third column of Table 2. As seen, there are large discrepancies between our values and the values for $\Delta_{sol}H$ reported by Yin et al.[21,] particularly for the C_{70} systems. We believe that this arises from the fact that the fullerene samples

are handled in open ampules exposed to the solvent vapor in the solution calorimeter used by Yin et al. Solvates stable at room temperature may have formed, and probably part of the fullerene sample was converted to solvate by taking up gaseous solvent during the equilibration period.

Methyl groups as substituents increase the interaction with C_{60} as indicated by an increasingly more exothermic solution enthalpy in the series toluene, 1,2-dimethylbenzene, 1,2,4-trimethylbenzene. Likewise, the dissolution of C_{70} is more exothermic in 1,2-dimethylbenzene than in toluene. The change from methyl groups to chlorine atoms does not have any drastic influence on the interaction as shown by the solution enthalpies that are almost the same in 1,2-dimethyl- and 1,2-dichlorobenzenes for both fullerenes. The solution enthalpy of both C_{60} and C_{70} in 1,3-dichlobenzene is less exothermic than for 1,2-dichlorobenze by 1.5 kJ mol⁻¹. Thus, the change in substituents from methyl to chlorine and the change from the 1,2- to the 1,3-position in the dichlorobenzene have about the same effect on $\Delta_{sol}H$ of the two fullerenes.

The stronger interaction of C_{70} with aromatic solvents than C_{60} as shown by the more exothermic solution enthalpies may just reflect the larger number of unsaturated carbon−carbon bonds in C_{70}.

Some details of the results for certain binary systems are discussed below.

C_{60}−Benzene: Orientational Phase Transitions in Solvates. The C_{60}−benzene solvate with a composition 1:4 has been previously described.[17,18] Seven samples with a molar ratio of C_{60} to benzene from 1:2.5 to 21.7 were examined. We observed incongruent melting or decomposition of this solvate at 322 K with an enthalpy change of 41 ± 1 kJ/mol of C_{60}. The composition determined from DSC measurements was 3.8 ± 0.2 mol benzene per C_{60}. He et al.[22] concluded from their room-temperature NMR measurements that in the 1:4 solvated crystal with benzene the rotation of the C_{60} units is not hindered. On the other hand, single-crystal X-ray data of Meidine et al.[17] at 173 K showed that the C_{60} molecules are locked and that no rotation is possible. It is interesting to note that no peak corresponding to the orientational phase transition was detected in our DSC experiments from 173 K up to the incongruent melting point of the solvate at 322 K. Neither were peaks of orientational phase transitions detected in other systems. The only exception could be a small peak found in the system C_{60}−1,3-dimethylbenzene at 332 K (see Table 1).

C_{60}−Toluene: Decomposition through a Metastable Intermediate Phase? Five samples were studied with molar ratios of C_{60} to toluene between 1:2.3 and 1:10.1. After conditioning of the samples for 3−6 h at 250 K DSC traces from temperature upscans at a rate of 2.5 K/min showed no indication of the C_{60} phase transition peak at 259 K but a new narrow peak at 285.0 ± 0.2 K. The area under the symmetric peak corresponded to an enthalpy change of 19 ± 1 kJ/mol of C_{60}, which was attributed to the decomposition of solvate **I** of C_{60} with toluene. Measurements of 12 samples with molar ratios of C_{60} to toluene from 1:2.5 to 1:80 confirmed the presence of a peak at 285 ± 1 K corresponding to an enthalpy change of 20 ± 2 kJ/mol of C_{60}. The stoichiometry of the solvate was determined to 1:(1.8 ± 0.5) using the method of the Tammann triangle.[23] More careful measurements at temperatures above 285 K using higher scanning rates showed the presence of another peak around 320 K. With a scanning rate of 10 K/min we observed $T_{max} = 322 ± 1$ K and $\Delta H = 10 ± 2$ kJ/mol. The shape of the peak at 322 K depended on the scanning rate, becoming broader with decreasing rate and then disappearing at 2.5 K/min or lower,
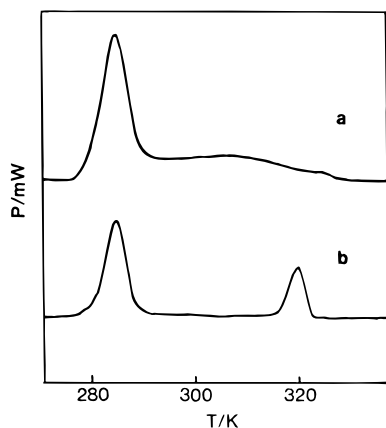
Figure 1. DSC curves for the system C$_{60}$−toluene from upscan at a scanning rate of (a) 2.5 K/min and (b) 10 K/min. The ordinate label *P*/mW stands for thermal power in milliwatts.

while the peak at 285 K was unchanged (see Figure 1). If samples were prepared at room temperature, no peak at 322 K was observed. The following experiment illuminated the nature of the peak at 322 K. A sample with the molar ratio of 1:4 was kept at 265 K for several days before being heated in the DSC up to 298 K and held at this temperature for 30 min. This first scan showed as expected the pronounced peak at 285 K. A second DSC scan from 273 K up to 350 K was run immediately after the temperature had been decreased to just below 270 K. Only the peak at 322 K was seen in this second scan. However, if in the same type of experiment the sample was allowed to stay at room temperature for 2 days instead of 30 min, the peak at 322 K disappeared. We believe the peak at 322 K corresponds to the incongruent decomposition of a second solvate (**II**), which contains less than 2 moles of toluene per mole of C$_{60}$. Solvate **II** would be a metastable intermediate that would decompose spontaneously but slowly at room temperature. An alternative explanation is that the solvate decomposes at 285 K according to reaction 3 but gives C$_{60}$ in a rearranged, metastable form that would relax to the stable form as the temperature is increased. When the solvate forms, the arrangement of the C$_{60}$ molecules probably changes from a simple cubic structure with 12 nearest neighbors to a structure with a lower number of fullerene neighbors in the solvate.[7] The true equilibrium phases above 285 K should be C$_{60}$(s) and its saturated solution. We note that the change of the slope of ln *x* against 1/*T* at the maximum solubility temperature 285 K corresponds to an enthalpy change of 35 kJ/mol, which is close to the sum of the effects at 285 and 322 K and much larger than the effect at 285 K alone. It might be assumed that under equilibrium conditions the 1:2 solvate will completely decompose at 285 K to give solvent-free C$_{60}$ with an enthalpy change of 30−35 kJ/mol.

Polymorphism in C$_{60}$−1,2-Dichlorobenzene and C$_{60}$−1,2-Dimethylbenzene. The first upscan of fresh samples of C$_{60}$−1,2-dichlorobenzene demonstrated a well-shaped peak at 322 K, giving an enthalpy change of 18.5 ± 2.3 kJ/mol (see Figure 2a). However, if the same samples were left to stand at 260 K for 48 h a broad peak with two equally high maxima at 320 and 340 K were observed (Figure 2b). After another 48 h the peak around 340 K became much larger. After 2 months the first upscan showed only a peak at 342 K, giving an enthalpy change of 19 ± 2 kJ/mol (Figure 2c). In a subsequent upscan only the peak at 320 K was seen. Fresh samples prepared by precipitation of the solvate from the saturated solution at room temperature showed only the peak at 340 K in the first upscan. We interpret these experiments to indicate that two polymorphic
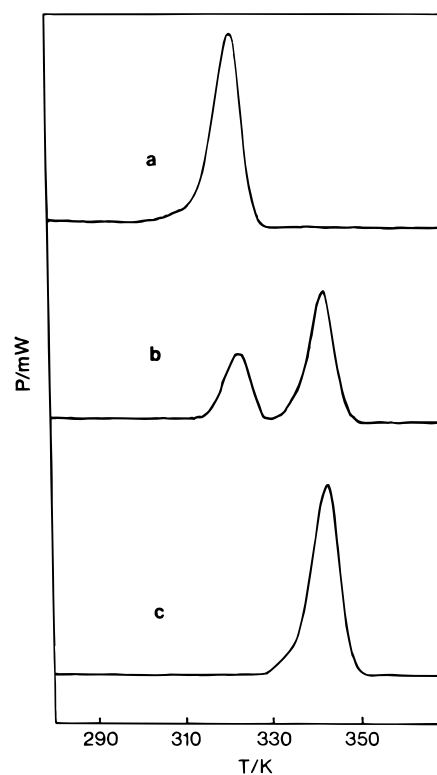
Figure 2. DSC curves for the system C$_{60}$−1,2 dichlorobenzene showing the formation of two polymorphic forms of the solvate: (a) fresh sample; (b) after 48 h at 260 K; (c) 2 months after preparation of the sample. Curves are from upscans at a rate of 10 K/min. The ordinate label *P*/mW stands for thermal power in milliwatts.

forms of the solvate are formed. Both have the same enthalpy but different entropies of formation, 55 and 59 J/mol K, for the high-temperature and low-temperature forms, respectively. The metastable low-temperature phase transforms into the more stable high-temperature phase with time, which takes days if the sample is kept at 260 K. Such monotropic polymorphic transitions are frequently observed for organic substances.[24] A similar but less pronounced effect was seen in the system C$_{60}$−1,2-dimethylbenzene. Here, the difference between the two temperatures for the incongruent melting did not exceed 10 °C.

Binary Systems of C$_{60}$ and C$_{70}$ with 1,2- and 1,3-Dimethylbenzene and with 1,2- and 1,3- Dichlorobenzene: Similar Interaction with Similar Isomers? The data on the incongruent melting transition found in the binary systems of C$_{60}$ or C$_{70}$ with the 1,2- and 1,3-derivatives of dimethyl- and dichlorobenzene are presented in Table 1. Both 1,2-dimethyl- and 1,2-dichlorobenzene form 1:2 solvates with C$_{60}$. In the systems of the 1,3-derivatives, C$_{60}$ forms two solvates. No solvate was detected in the systems of C$_{70}$ and the 1,3-derivatives, while two solvates were observed with 1,2-derivatives. Thus, the position of the substituent groups, −Cl or −CH$_3$, determines the type of solvate that is formed. The position of the substituents also has a strong influence on the solubility; for instance, C$_{60}$ is much more soluble in 1,2-dimethyl- and 1,2-dichlorobenzene than in the 1,3-substituted benzenes[8] (see below and Table 4). The entropies of incongruent melting of similar solvates of C$_{60}$ and C$_{70}$ with 1,2-dimethyl- and 1,2-dichlorobenzene are surprisingly different (see Table 1).

Comparison with the Solubility Data. For five of the systems in our study the solubility has been determined over wide temperature ranges, which makes possible the comparison between solubility data and results in our study. The systems

TABLE 3: Temperatures of Maximum Solubility and Enthalpies of Reaction and Solution Derived from the Temperature Variation of Solubility and Calorimetric Measurements

fullerene−solvent	T_{max} K	T_{imp} K	$\Delta_r H$(vH) kJ/mol	$\Delta_r H$(DSC) kJ/mol	$\Delta_{sol}H$(vH) kJ/mol	$\Delta_{sol}H$(cal) kJ/mol
C_{60}−toluene	278[a]	285	35[a,b]	30	−12 ± 2[a,b]	−8.5 ± 0.7
C_{60}−1,2-dimethylbenzene	303[c]	322	34[d]	31	−11.6[d]	−14.53 ± 0.30
C_{60}−1,2-dichlorobenzene	310[e]	322	24[e]	19	−13.3[e]	−14.00 ± 0.15
C_{70}−1,2-dimethylbenzene	(280)[d,f]	282	11[d]	18		−18.84 ± 0.31
C_{70}−1,2-dichlorobenzene	328[e]	335	23[e]	8	−13.6[e]	−18.67 ± 0.17

[a] From ref 1. [b] From ref 4. [c] From ref 2. [d] Calculated in this study using data from ref 2. [e] From ref 3. [f] Change in slope but no maximum, solubility measured up to 353 K. Notes: T_{max} is the temperature of maximum solubility. T_{imp} is the incongruent melting point of a corresponding solvate. $\Delta_r H$(vH) is the van't Hoff enthalpy of reaction 3, calculated from the change of the slope of solubility curve at T_{max}. $\Delta_r H$(DSC) is the enthalpy of reaction 3 as measured by DSC. $\Delta_{sol}H$(vH) is the van't Hoff enthalpy of solution of fullerene. $\Delta_{sol}H$(cal) is the enthalpy of solution measured by calorimetry.

TABLE 4: Solubilities and Entropies of Solution Recalculated to Pure Fullerenes and Enthalpies of Solvation of C_{60} and C_{70} at 298 K

solvent−fullerene	$10^4 x^a$ [ref]	$10^4 x$(hyp)[b]	$-\Delta_{sol}S$(hyp)[c] J/(mol K)	$-\Delta_{solv}H^d$ kJ/mol
toluene−C_{60}	4.2 [8,9]	4.2	95.5	191
benzene−C_{60}	2.0 [8,9]	6.9		
1,2-dimethylbenzene−C_{60}	14.7 [8]	37.7	87.7	194
1,3-dimethylbenzene−C_{60}	3.6 [8,25]	10.4		
Bromobenzene−C_{60}	4.4 [8,9]	54.6	81.9	194
1,2-dichlorobenzene−C_{60}	38.3 [8,9]	102.2	86.6	196
1,3-dichlorobenzene−C_{60}	3.8 [8]	19.7	92.0	194
1,3,5-trimethylbenzene−C_{60}	3.3 [8]	41.6		
1,2,4-trimethylbenzene−C_{60}	33.5 [8]	105.7	96.6	199
1,2-dimethylbenzene−C_{70}	22.3 [2]	130.5	99.3	219
1,2-dichlorobenzene−C_{70}	34.6 [3]	446.9	88.5	219

[a] Measured solubility x (mole fraction). [b] Solubility x(hyp) relative to pure fullerene (see eq 4 and text). [c] Hypothetical entropy of solution calculated according to eq 5. [d] Enthalpy of solvation calculated according to eq 6.

are shown in the first column of Table 3. The observed temperature T_{max} for the maximum in the solubility is given in the second column, which should correspond to the temperature for the incongruent melting of the solvate T_{imp} shown in the third column. The enthalpy change for the decomposition of the solvate, reaction 3, can be estimated from the variation of the solubility with temperature using the integrated forms of the van't Hoff eqs 1 and 2. The section below T_{max} will give an estimate of the van't Hoff solution enthalpy for the solvate $\Delta_{sol}H(C_x \cdot nB)$(vH) and above T_{max} of $\Delta_{sol}H$(vH) assuming that the solid phase is pure C_x. $\Delta_{sol}H(C_x \cdot nB)$(vH) minus $\Delta_{sol}H$(vH) gives the van't Hoff reaction enthalpy $\Delta_r H$(vH). The temperature dependence of the solution enthalpies was neglected. The derived values of $\Delta_r H$(vH) are shown in the fourth column, and they can be compared with the values determined from the DSC experiments in the fifth column. Derived values of $\Delta_{sol}H$(vH) are given in the sixth column and the solution enthalpies $\Delta_{sol}H$(cal) determined from calorimetric measurements at 298 K in the last column. The uncertainty in the values of the solution enthalpies derived from the solubility measurements is probably on the order of 3 kJ/mol at the mean temperature of the interval used.

In all the systems where a solubility maximum was observed, the incongruent melting of a solvate was detected by DSC just above T_{max}. This confirms once again that the formation and incongruent melting of solid solvates are the cause of the abnormal temperature dependencies of solubility. The directly measured values for the enthalpy of solution of C_{60} in toluene and 1,2-dimethyl- and 1,2-dichlorobenzene agree well with the derived van't Hoff values considering the uncertainties. This strongly indicates that the solid phase above T_{max} is pure C_{60}. Further, the enthalpy changes for the incongruent melting of solvates of C_{60} determined from DSC experiments agree well with the estimated values from the solubility measurements.

In the system C_{70}−toluene, where no solvate was identified below the normal boiling point of toluene, only a slight increase of solubility with no maximum was found.[2] However, the solubility of C_{70} in 1,2-dimethylbenzene showed a pronounced increase with temperature, signifying an endothermic solution enthalpy.[2] This must arise from a solvate, since we found the enthalpy of solution of pure C_{70} to be −18.8 kJ/mol. This was confirmed by the finding in the DSC experiments of a solvate decomposing at 367 K (see Table 1). Most likely, a maximum in the solubility will be observed around this temperature if the range of measurements were extended. There is a distinct change of slope around 280 K of the solubility curve of C_{70} in 1,2-dimethylbenzene, which can be correlated with the transition peak observed in the DSC experiments at 283 K (see Table 1). A low-temperature solvate containing three to four solvent molecules rearranges and loses several solvent molecules with an enthalpy change of 18.5 kJ/mol as determined from the DSC peak. This second solvate then decomposes to give pure C_{70} around 369 K.

In the C_{60}−1,2-dichlorobenzene system the metastable solvate with the lower incongruent melting point most likely is the form present during the solubility measurements.[3] We found that the more stable solvate in this system required at least a couple of weeks to form, which is a much longer time than the duration of the solubility experiment (see Table 1). For the system C_{70}−1,2-dichlorobenzene the reaction enthalpy determined by DSC is only one-third of the van't Hoff value. It is not clear if the discrepancy indicates that the solid phase above T_{max} is a second solvate and not pure C_{70} or if it is due to large uncertainties in the values.

Absolute Values of Solubility. The formation of solid solvates makes one reconsider room-temperature solubilities of C_{60} and C_{70} published in the literature, since these solubilities are concentrations of fullerene in the solutions saturated relative

to different solid phases (different solvates or solid C_{60} or C_{70}). To discuss solubilities, it may be better to compare saturation concentrations relative to the same solid phase, namely, to pure C_{60} or C_{70}, though in many systems this solid phase is metastable at room temperature. The following equation, derived by integration from eqs 1 and 2, was used to recalculate the solubilities:

$$\ln[x(\text{hyp})/x] = (\Delta_r H/R)(1/298 - 1/T_{\max}) \qquad (4)$$

where x is the measured saturated mole fraction of C_{60} or C_{70} at 298 K, $x(\text{hyp})$ is the mole fraction of $C_{60}(C_{70})$ in the hypothetical solution, saturated relative to solid C_{60} or C_{70} at 298 K, and $\Delta_r H$ denotes the enthalpy of reaction 3. Equation 4 is applied consecutively if two solvates are formed in the system above 298 K.

Experimentally measured and recalculated solubilities of C_{60} and C_{70} at 298 K in a number of aromatic solvents are presented in the third column of Table 4. The experimentally determined solubilities chosen for this comparison are shown in the second column. Entropies of solution $\Delta_{\text{sol}}S(\text{hyp})$ given in the fourth column of Table 4 were calculated using the equation

$$\Delta_{\text{sol}}S(\text{hyp}) = R \ln x(\text{hyp}) + \Delta_{\text{sol}}H/T \qquad (5)$$

Enthalpies of solution were taken from Table 2.

The recalculations of solubility did not change the general impression, which is that there is no obvious order in the data of Table 4. It is true that the recalculated values show the solubility to increase with increasing number of methyl substituents. However, the large influence of the position of the substituents persists as shown by the large difference between the solubility of C_{60} in 1,2- and 1,3-dimethylbenzene and 1,2,4- and 1,3,5-trimethylbenzene. Also, for 1,2- and 1,3-dichlorobenzene there is a large difference between the solubilities of C_{60}. The solubility is lower in the systems in which more stable solvates form. The enthalpies of solution appear not to vary to the same extent with the position of the substituents (see Table 2). In the recalculations of solubilities we assume that the solid phase in equilibrium with the solution consists of the pure fullerene above the highest transition temperature we observe in the DSC experiments. Most likely, pure fullerene is the equilibrium phase above $T_{\max}$ in systems for which maxima in solubility have been observed (see Table 3). However, for the systems of 1,3- dimethyl -and 1,3-dichlorobenzene and 1,3,5-trimethylbenzene with C_{60} we have no information about the high-temperature composition, and it is possible that the solid-phase still is not pure C_{60} but a solvate.

Both fullerenes have a solubility that is well below the values predicted by the ideal solution model or the Hildebrand regular solution model. If one assumes that the temperature and entropy of melting of C_{60} are 1200 K and 10.5 J/K mol, respectively,[26] the resulting solubility at 298 K would be 0.0206. *The critical factor that diminishes the solubility is the negative entropy of dissolution, which is between -80 and -100 J/mol K for both C_{60} and C_{70} in the solvents studied* (Table 4).

The enthalpy of solution $\Delta_{\text{sol}}H$ can be expressed as a sum of the enthalpy of sublimation $\Delta_{\text{sub}}H$ and the enthalpy of solvation $\Delta_{\text{solv}}H$:

$$\Delta_{\text{sol}}H = \Delta_{\text{sub}}H + \Delta_{\text{solv}}H \qquad (6)$$

The solvation enthalpy $\Delta_{\text{solv}}H$ represents the change of enthalpy in the process of transferring individual fullerene molecules into solution from the gas phase. The sublimation enthalpies C_{60} and C_{70} are equal to 182 ± 3 kJ/mol[27] and 200 ± 6 kJ/mol,[28] respectively. The resulting $\Delta_{\text{solv}}H$ is more negative for C_{70} than for C_{60} in the same solvent (see Table 4). The ratios of solvation enthalpies $\Delta_{\text{solv}}H$ for C_{70} and C_{60} in both 1,2-dimethylbenzene and 1,2-dichlorobenzene are close to 1.1, the ratio of the van der Waals surfaces of C_{70} and C_{60}.[29]

Conclusions

Solid solvates of C_{60} are easily formed in binary systems with aromatic solvents. Metastable forms of solvates were detected in a number of systems. Our DSC results indicate that C_{70} forms solid solvates less often. However, stable solvates that would decompose above the normal boiling point of the solvent were not detected by this method.

The solubility is determined by the solid phase in equilibrium with the solution and the temperature dependence of the solubility by the enthalpy of solution of the solid. Observed maxima in the solubility of C_{60} are caused by the incongruent melting of solvates to give pure C_{60} as the solid phase above the transition temperature. Enthalpies of solution of C_{60} and C_{70} in aromatic solvents are significantly exothermic, which gives a decrease in solubility with increasing temperature.

The low solubility of C_{60} and C_{70} in aromatic solvents is caused by a negative entropy of solution. The peculiarities of the absolute values of solubility of C_{60} and C_{70} cannot be explained by formation of solvates only. We have shown that even after the difference caused by the formation of solvates was taken away, the solubility of C_{60} in the positional isomers 1,2- and 1,3-dimethylbenzene and 1,2- and 1,3-dichlorobenzene was still significantly different.

The trends in the thermodynamic data for aromatic solid solvates of fullerenes, especially in entropies of formation, are far from clear. More X-ray and probably solid NMR data are needed in order to understand them.

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