SOLID SOLVATES OF C_{60}
Compositions and thermodynamics

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Abstract

Compositions of the solid solvates of C_{60} with 1,2-dichlorobenzene and 1,3,5-trimethylbenzene were determined with the help of experimental procedures developed. Possible correlations between compositions and thermodynamic properties were discussed.

Keywords: fullerene, solubility, solvates

Introduction

Solid solvates of fullerenes C_{60} and C_{70} with the corresponding solvents play a significant role in the solubility phenomena. Formation of solvates were reported by a number of groups. The solvates have been investigated by many experimental techniques, such as Differential Scanning Calorimetry (DSC) [1–11], heat capacity measurements [8,11], solution calorimetry [6, 7], X-ray (powder) [1–3, 12–15] and X-ray (single crystal) [6, 16, 17] diffraction, solid state nuclear magnetic resonance (NMR) [11, 18].

The determination of composition of solvates presented a significant problem in a number of cases. Though the solvates in question are thermodynamically stable phases at room temperature/normal pressure, the equilibrium vapour pressure of the solvent above the solvate could be high enough, which leads to the low 'kinetical' stability of the solvates and possible uncontrolled loss of the solvent from the dried samples. In some cases it is still even not clear, whether the solid solvate with fixed composition or solid solutions with variable composition are formed.

In this situation the conventional methods of determination of composition (chemical analysis, thermogravimetric measurements with dry samples) become ineffective, since it is not possible to control the starting material.

In the present study the attempt was made to develop simple reliable methods to overcome this difficulty. Two solvates of C_{60} with 1,2-dichlorobenzene and with 1,3,5-trimethylbenzene, both with disputable composition, were under careful examination.

Experimental

Materials

Samples of C_{60} were form MER Ltd. (99.9% mol). No additional purification was performed. 1,2-dichlorobenzene and 1,3,5-trimethylbenzene were commercial

samples from FLUKA with the stated purity 99%. The melting points measured with DSC for all the solvents were close (± 0.2 K) to the known literature values.

DSC measurements

The instrument used was DSC-30 Mettler. Measurements were taken at temperatures from 200 K up to 390 K in the nitrogen atmosphere. The scanning rates were 10 or 5 K min^{-1}. Heterogeneous (solid/liquid) samples with different mole ratios of C$_{60}$ to the solvent were studied. Mole ratio of solvent to fullerenes were less than 15 in the most of the samples. With such a ratio more than 98 per cent of fullerenes were kept in the solid phase rather than in the saturated liquid solution.

TG measurements

Thermogravimetric (TG) measurements were performed on Mettler thermobalance. Details of the experimental procedure are presented below.

Results

System C$_{60}$–1,2-dichlorobenzene

10–15 mg of C$_{60}$ was desolved completely in 1,2-dichlorobenzene and the solution was left to stand open in the dark for 3–7 days until the solid phase precipitated from the liquid. This solid phase with the mother liquor was scanned up with DSC in the sealed pan. The DSC trace showed the presence of the incongruent melting point at $T=342\pm2$ K with the enthalpy of the endothermic effect equal to 18 ± 1 kJ mol^{-1} of C$_{60}$. These temperature and enthalpy corresponded to the thermodynamic parameters of the incongruent melting of the solvated crystal, formed in the binary system C$_{60}$-1,2-dichlorobenzene [7]. The peak, corresponded to the orientational phase transition in C$_{60}$ at $T=259$ K was not detected. Based on these measurements it was decided, that C$_{60}$ was completely converted into the solvate and no pristine C$_{60}$ was left in the sample. Then the same sample (solvate+mother liquor) was taken for TG measurements. Integral and differential TG curves of the isothermal ($T=313$ K) run are presented in Fig. 1. As it is seen from the differential curve there was a pronounced change of the slope in the period of time from 45 up to 60 min after the beginning of the run. Change of the evaporation rate corresponded to the moment, when the liquid phase was evaporated completely and the evaporation of the solvent, incorporated into the solvate started. The isothermal run was continued up to the moment, when the sample stopped to lose mass. Then the temperature was raised up to 520 K. No additional loss of mass was detected. Dry sample of C$_{60}$, which was left after the run, was weighed. The amount of solvent, incorporated into the solvate, was determined from the loss of mass at the period of time from 50 up to 120 min. The same experimental procedure was used with the two other samples in the system C$_{60}$-1,2-dichlorobenzene. The resulting composition of the solvate (averaged value of three experiments) was 1:1.9$\pm$0.2 (C$_{60}$ to 1,2-dichlorobenzene, molar ratio). It is
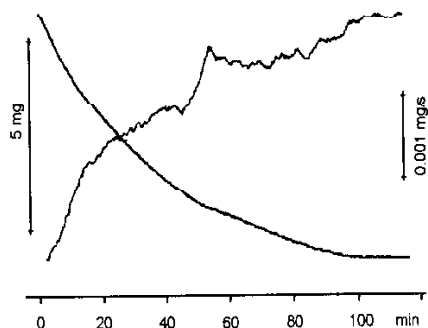
Fig. 1 TG isothermal scan of the {C60-1,2-dichlorobenzene} sample

worth noting that our attempts to employ the conventional TG procedures with the preliminary dried samples (solid solvate only, no mother liquor!) led to irreproducible results due to spontaneous loss of the solvent, incorporated into the solvent.

The composition of the solvate was also determined with DSC. The same accurately weighed mixture of the solid solvate with the mother liquor was scanned in the sealed pan. The amount of nonbound 1,2-dichlorobenzene was determined from measurements of the peaks arising from the freezing or melting of the excess solvent in the DSC scans (Fig. 2). After the run the solvent was completely removed from the sample and the pristine C_{60} was weighed.
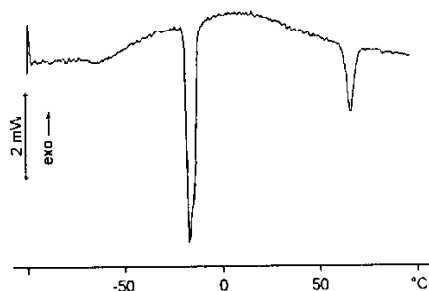

Fig. 2 DSC scan of the {C60-1,2-dichlorobenzene} sample. Rate=10°C min⁻¹

Measurements with five samples gave the composition 1:2.0±0.5. DSC procedure, compared to the TG procedure described above, was much more convenient, but less accurate.

C_{60}-1,3,5-trimethylbenzene

Samples were prepared and checked similarly to the case of 1,2-dichlorobenzene. The solvate with 1,3,5-trimethylbenzene is comparatively more stable, which allows one to perform more conventional TG upscan. The evaporation of a free liq-

uid and bound 1,3,5-trimethylbenzene were separated in time and in temperature. The amount of solvent, incorporated into the solvate was determined from the second, high temperature peak (Fig. 3). Measurements with the three samples gave the composition 1:0.5±0.2.
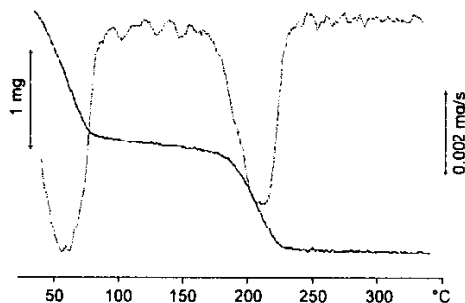

Fig. 3 TG scan with the sample from the system {C$_{60}$-1,3,5-trimethylbenzene}. Rate=10°C min^{-1}

The DSC procedure, described above was not applicable in case of 1,3,5-trimethylbenzene due to the reported formation of the second, low temperature solvate in this system [7].

Discussion

The available information on the solid solvates of C$_{60}$ with the aromatic solvents is summarized in Table 1.

The certain solvate could suffer one of the two isothermal transitions, namely, of incongruent melting:

$$C_{60} \cdot nL_{(s)} = nL_{(liq)} + C_{60(s)} \tag{1}$$

or of desolvation

$$C_{60} \cdot nL_{(s)} = nL_{(gas)} + C_{60(s)} \tag{2}$$

depending upon whether the incongruent melting occurs below or above the normal boiling point of the solvent, respectively. (L is a solvent, n-molar ratio of solvent to C$_{60}$ in the solvate).

The compositions of the solvates are presented in the second column of the Table.

Temperatures of the incongruent melting or desolvation (in the case of the high temperature solvate of C$_{60}$ with 1,3,5-trimethylbenzene) are given in the third column.

The fourth one contains enthalpies of the reaction (1) for all of the solvates. The numbers in brackets are the enthalpies of the reaction (1) per mole of a solvate, i.e. $\Delta H/n$.

Table 1 Thermodynamics and composites of the solid solvates of C_{60} with the aromatic solvents

Solvent	Composition of solvates (C_n:solvent)	$T/$ K	$\Delta H_{(1)}/$ kJ mol^{-1}	$\Delta S_{(1)}/$ J (mol K)$^{-1}$	$\Delta G_{(298K)}/$ kJ mol^{-1}	$p/$ kPA
toluene [7]	1:1.8±0.2	285±1	30±2	105		
	(1:2)		(15)	(50)		
1,2-dimethylbenzene [7]	1:2.11±0.18	322.0±2.6	31.3±1.4	97	2.3	0.5
	(1:2)		(15.5)	(43)		
1,2-dichlorobenzene	1:0.9±0.2	342	18.5±2.3	55	2.4	0.11
			(9)	(28)		
1,3,5-trimethylbenzene	?	292–300	25–44	146	6.4	0.0008
	1:0.5±0.2	460.8±1.5	16.3±0.5	33		
			(33)	(66)		
bromobenzene [6]	1:2	350±1	42±2	120	6.2	0.2
			(21)	(60)		

Table 1 also includes entropies of the reaction (1) (the fifth column) calculated by using the relationship

$$\Delta S_{(1)} = \Delta H_{(1)}/T,$$

valid at the transition temperature.

The sixth column contains $\Delta G_{(298K)}$ of the reaction (1), calculated by under the assumption that both $\Delta H_{(1)}$ and $\Delta S_{(1)}$ are temperature independent of room temperature up to the decomposition temperature of the solvate. With the knowledge of $\Delta G_{(298K)}$ and of the saturated vapour pressure of the solvent at room temperature (P) [19], it was possible to calculate the decomposition vapour pressure (p) of a solvent over a solvate at room temperature (the seventh column) according to the equation

$$\ln_p = -\Delta G_{(298K)}/RT_n + \ln P$$

The pressure p characterizes the solvate's ability to survive without a mother liquor. (Note that 1:2 solvate with toluene decomposes below room temperature. $\Delta G_{(298K)}$ for it is not given.)

As it is seen from the Table the enthalpy and the entropy of the reaction (1) for the solvate with 1,2-dichlorobenzene are significantly lower, compared to the cases of toluene, 1,2-dimethylbenzene and bromobenzene. That was one of the reasons why we wanted to check the composition of the former solvate. The compositions, however, appeared to be the same in all four cases. The explanation of the unusual properties of 1,2-dichlorobenzene solvate could probably be found in its X-ray structure.

The binary system of C_{60} with 1,3,5-trimethylbenzene gives the first example of a solvate with the composition 1:0.5. Only solvates with the compositions 1:2 and 1:4 were reported in the literature so far.

The 1:0.5 solvate with 1,3,5-trimethylbenzene is the most kinetically stable aromatic solvate of C_{60}. Due to low decomposition pressure, it has not lost solvent at room temperature.

<p style="text-align:center">* * *</p>

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