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THERMODYNAMIC PROPERTIES OF THE MOLECULAR COMPLEXES OF C_{60} WITH MONOSUBSTITUTED NAPHTHALENES

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The binary systems of C_{60} with α-methyl- and α-chloronaphthalene have been studied by means of differential scanning calorimetry. C_{60} was found to form the molecular complex of the van der Waals type with α-methylnaphthalene which melts incongruently below the boiling point of the solvent at temperature 382.7±3.0 K. The enthalpy of the desolvation reaction is 14.1±0.5 kJ mol^{-1} of C_{60}. The molar ratio of fullerene to solvent in the solvate is 1:1.5. In the system C_{60}–α-chloronaphthalene a two-stage incongruent melting process has been observed at temperatures 314.1±4.6 K and 375.7±7.4 K with the enthalpies 8.1±2.6 kJ mol^{-1} and 11.6±1.0 kJ mol^{-1}, respectively. The composition of the most solvated phase equilibrated with the saturated solution at room temperature and below the first of the incongruent melting transitions was determined as 1:1.5. Based on the results obtained the thermodynamic characteristics of the incongruent melting reactions have been revealed and influence of solvate formation on solubility of C_{60} has been discussed.

Keywords: *DSC, fullerenes, solvates, stability, thermodynamics*

Introduction

The formation of solid solvates with different classes of solvent molecules (aromatics, alkanes, halogenated alkanes and etc.) is a characteristic feature of fullerenes. Dramatic changes in crystalline lattice and decomposition (incongruent melting) of these van der Waals complexes result in anomalous temperature dependence of solubility [1, 2]. Absolute values of solubility of fullerenes also depend upon the thermodynamic stability of these solids. The type of crystalline lattice, 'characteristic compositions', and the type of the phase diagrams were shown to be influenced essentially on the shape of the guest molecules [1, 3]. Monosubstituted naphthalenes were shown to be among the best solvents for fullerenes. The experimental room temperature solubilities of C_{60} in α-chloronaphthalene and α-methylnaphthalene are 51 and 33 mg mL^{-1}, respectively [4]. However, practically little is known about the thermodynamic stability of the phases equilibrated with the saturated solutions [5]. DSC technique was successful used to study the nature of solvates [6–9]. In the present study measurements were carried out for the systems of C_{60} with α-chloronaphthalene and α-methylnaphthalene.

Experimental

Samples of C_{60} were obtained from Bucky USA (99.5%) and Fullerene Technologies, St. Peterburg, Russia (99.0%). The solvent α-methylnaphthalene was a commercial sample of >97% purity from Lancaster, α-chloronaphthalene was a commercial sample with the trademark HP. Both solvents were used without additional purification. DSC-30 Mettler instrument was used to record DSC traces. Several samples with different molar ratios of C_{60} to solvent were studied. Each sample was scanned several times and was kept at room temperature (293–298 K) before measurements. The scanning rate was 10 K min^{-1}. Further details of the experimental procedure were described elsewhere [1].

Results and discussion

C_{60}–α-methylnaphthalene

Several heterogeneous samples with different molar ratios of C_{60} to solvent prepared by adding of certain amount of α-methylnaphthalene to known quantity of fullerene were scanned in hermetically sealed pans. Before measurements the samples were left at room temperature for several days. The new endothermic peak observed in the DSC traces (up scans) at 382.7±3.0 K (onset temperature) with the corresponding enthalpy change 14.1±0.5 kJ mol^{-1} of C_{60} was attributed to the incongruent melting of the solid solvate of C_{60} with α-methylnaphthalene. The endothermic peak corresponding to melting of the excess solvent that was present in the sample but was not incorporated into the solid solvate was seen in the DSC trace as well.

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The peak of the orientational phase transition of C_{60} at 260 K normally observed for pure fullerene completely disappeared from the DSC traces. According to our previous experience [1] this indicates to the complete conversion of C_{60} to another phase, namely molecular complex of C_{60} with the solvent. However, for one of the samples with the molar ratio of C_{60} to solvent 1:1.35 the small peak of orientational phase transition at 260 K was still present in the the trace besides the endotherm at 383 K. There was no indication to the presence of the 'extra' solvent in the system (absence of the peak of a solvent melting). This means, that more solvent is needed to form the equilibrium solid phase. Using the simple mass balance equations the composition (fullerene to solvent molar ratio) in the solvate was found to be 1:1.5 (±0.1). The entropy of incongruent melting reaction

$$C_{60}\cdot 1.5C_{10}H_7CH_3(s)=C_{60}(s)+1.5C_{10}H_7CH_3(liq) \quad (1)$$

calculated as a change of entropy for the phase reaction, $\Delta_rS=\Delta_rH/T$, was found to be 37 J mol^{-1} K^{-1}.

In spite of the essential modification of the C_{60} absorption spectra in solution [10] the enthalpy of incongruent melting of the complex per one mole of a solvent is only 10 kJ mol^{-1} which is even less than the typical values for the aromatics (derivatives of benzene) (15–20 kJ mol^{-1} [1]). The results of the present study may be compared with the data obtained in the earlier work [10]. Based on the results of their TG and DSC experiments, the authors [10] have reported the formation of a 1:1 solvate in the system under consideration. The enthalpy of decomposition reaction with the formation of gaseous solvent was found to be equal to 79.2 kJ mol^{-1}. This enthalpy change exceeded evaporation enthalpy of the pure solvent. One may calculate the incongruent melting enthalpy (reaction (1)) by subtracting of average solvent evaporation enthalpy from the experimental decomposition enthalpy reported by Kowalska [10]. The value obtained (20 kJ mol^{-1}) does not differ considerably from the value obtained in the present study. However, the solvate compositions are different. Unfortunately, no details of the TG determination of a solvate composition were presented. Our direct experiment with the sample 1:1.35 (see above) confirmed, that more than 1.35 moles of α-methylnaphthalene per mole of C_{60} are incorporated into the solvate.

C_{60}–α-chloronaphthalene

The DSC experimental procedure was practically the same as in the previous case. The samples with molar ratios of C_{60} to solvent from 1:2.4 to 1:3.6 were studied. Two new endothermic peaks were found. The low temperature peak was rather broad and sometimes with the irregular shape. The corresponding onset temperature and the enthalpy change were 314.1±4.6 K and 8.1±2.6 kJ mol^{-1}, respectively. For the second broad peak the temperature and the enthalpy were 375.7±7.4 K and 11.6±1.0 kJ mol^{-1}, respectively. Two solids with different amounts of solvent molecules incorporated are thermodynamically stable in the certain temperature intervals. The applied procedure based on 'extra' solvent measuring allowed the determination of the composition of the 'low temperature', most solvated phase. The fullerene to solvent ratio was revealed as 1:1.4 (±0.3) with the absolute determination error three times higher compared to the previous system. The composition of the molecular complex ($C_{60}\cdot 1.5C_{10}H_7Cl$ (*s*)) is the same as in case of α-methylnaphthalene. The composition of the high temperature solvate ($C_{60}\cdot mC_{10}H_7Cl$ (*s*)) was not determined. The incongruent melting processes are presented below:

$$C_{60}\cdot 1.5C_{10}H_7Cl\,(s)= C_{60}\cdot mC_{10}H_7Cl\,(s)+(1.4-m)C_{10}H_7Cl\,(liq) \quad (2)$$

$$C_{60}\cdot mC_{10}H_7Cl\,(s)=C_{60}\,(s)+mC_{10}H_7Cl\,(liq) \quad (3)$$

The entropies of decomposition for both processes (2) and (3) calculated as $\Delta_rS=\Delta_rH/T$ are equal to 26 and 31 J mol^{-1} K^{-1}, respectively.

Solubility behaviour

According to the results obtained in the present study the solid solvates rather than pure fullerene are equilibrated with the saturated solution at room temperature and up to the temperatures of incongruent melting in both of systems studied. One may estimate the influence of solvate formation on the fullerene solubility when calculating of the ratio of the so-called 'hypothetical' solubility (relative to pure, unsolvated C_{60}) to experimental one using the simple thermodynamic equation:

$$\mathrm{Ln}(x'/x)=\Delta_rH(1/T-1/T_r) \quad (4)$$

where x' and x are hypothetical and experimentally measured solubilities (molar fractions) at 298 K, respectively, ΔH and T_r are the enthalpy and the temperature of the incongruent melting reaction. According to Eq. (4) the recalculated solubility of C_{60} in α-methylnaphthalene is 3.5 times higher than the experimentally measured one. The same calculations were performed for the system of C_{60} with α-chloronaphthalene. In this case, however, two terms at the right side of Eq. (4), corresponding to the two incongruent melting reactions should be taken into account. The hypothetical solubility is 3.1 times higher than the experimentally measured one in this case. Table 1 contains experimental and recalculated (hypothetical) solubilities of C_{60} in α-methyl- and chloro-

Table 1 Experimental and recalculated solubilities of C_{60} in α-methyl- and α-chloronaphthalene and methyl- and chlorobenzene at 298 K

System	Reference	$x(\text{exp})10^4$	$x(\text{hyp})10^4$
C_{60}–α-$C_{10}H_7CH_3$	This study	69.0	240.0
C_{60}–α-$C_{10}H_7Cl$	This study	97.0	302.0
C_{60}–$C_6H_5CH_3$	[11]	4.2	4.2[a]
C_{60}–C_6H_5Cl	[11]	9.0	11.4

[a] the solvate decomposes below 298 K

naphthalene and in methyl and chlorobenzene adduced for comparison [4].

Based on the data presented in Table 1 one may conclude that Cl– substituted derivatives are more effective solvents than CH_3– substituted analogs. It is worth noting that the same is true for 1,2- and 1,3-disubstituted benzenes [11]. When going from benzene to naphthalene derivatives the solubilites increase significantly. That could be explained probably by more strong π–π interaction between electron deficient C_{60} fullerene cage and molecules of naphthalene derivatives, rich in π-electrons.

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