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THERMOCHEMISTRY OF C_{60} AND C_{70} FULLERENE SOLVATES

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In an effort to improve understanding of dissolution behaviour of fullerenes and their simple chemical derivatives the binary systems of C_{60}, C_{70} and the piperazine monoadduct of [60] fullerene C_{60} $N_2C_4H_8$ with a series of aromatic solvents have been studied by means of DSC. In certain systems solid solvates have been found to be the thermodynamically stable phases relative to saturated solution at room temperature. Identified solid solvates were characterized by their compositions, temperatures and enthalpies of incongruent melting transitions. The regularities in thermodynamic stability of the solvated crystals have been discussed along with dissolution properties of fullerenes and the derivative. Certain correlations have been observed.

Keywords: *$C_{60,}$ C_{70}, fullerene, thermochemistry of solvates*

Introduction

Solid solvates of fullerenes and their derivatives with the efficient, mostly aromatic solvents play a significant role in the solubility phenomena. The thermodynamic studies of solubility behaviour of C_{60} and C_{70} in the aromatic solvents proved that room temperature solubility is restricted by the formation of such solvates. The decomposition (incongruent melting) of these complexes was shown to be the reason for arising of temperature maximums of solubility [1–5].

The solvates are held together with weak, van der Waals interactions. No charge transfer, proved by changes in infrared spectra, was reported so far.

Being a globular molecule, C_{60} is an excellent candidate for checking of the different models of solute-solvent interactions and solubility [6–9].

Another intriguing feature of the solution behaviour of C_{60} is great difference in solubility at ambient temperature observed for positional isomers such as 1,2- and 1,3-dichlorobenzene and 1,2,4- and 1,3,5-trimethylbenzene. Chemical properties in the liquid phase of the two pairs of solvents are similar [2, 10].

DSC technique was successful used to study the nature of solvate [11–14].

This work was focused on experimental study of the binary systems of C_{60}, C_{70}, or $C_{60}N_2C_4H_8$ with the typical aromatic solvents. Their thermodynamic properties were studied by means of DSC. The solubility behaviour of fullerenes was correlated with the stability of the solid solvates formed in the system.

Experimental

Fullerene C_{60} was purchased from Bucky, USA (99.5% mol. purity) and Fullerene Technologies company, S. Petersburg, Russia (99% mol. purity). The solvents (1,2-dibromobenzene, 1,3-dibromobenzene, 1,2,4-trichlorobenzene, 1,3,5-trimethylbenzene) were commercial samples of the purity better than 99%. They were used without additional purification. Piperazine $C_4N_2H_{10}$ is a cyclic secondary amine. Nucleophilic addition to the electron deficient C_{60} produces mono-, bis-, and multi-adducts of C_{60}-piperazine. 950 mg of C_{60}-piperazine monoadduct was synthesized based on procedure of Kampe *et al.* [15]. Flash column chromatography (Silicagel 50 mm diam.×50 cm length, 100:1 methylene chloride/methanol eluent) was used to separate the monoadduct from C_{60} and the higher adducts. Elemental analysis, TG, FTIR and mass spectrometry showed the monoadduct as well as the presence of chlorinated solvents which could not be completely removed by heating the sample in vacuum at 170°C. Heating the sample to higher temperatures in vacuum produces sample degradation. Subsequently a number of times the synthesis Bolch [16] *et al.* reported using a 9.1 mixture of dichloromethane and methanol as mobile phase for HPLC separation of crude product mixture was repeated and analytical HPLC (PerkinElmer. Buckyclutcher analytical column) to characterize the purity of the mono-adduct with respect to do C_{60} and higher adducts as 97% was used. Sublimed sample of C_{70} (MER Corp > 99% mol. purity) of doubly after gentle grinding in an agate mortar was used.

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A DSC-30 Mettler instrument was used to capture DSC traces. Measurements were taken at temperatures from 180 to 670 K with the scanning rates 10 and 5 K min^{-1} (upscans and downscans). Several heterogeneous (solid-liquid) samples of the binary systems (fullerene+solvent) under study with the molar ratios of fullerene to solvent less than 1:15 were treated. With such a ratio, more than 98% of fullerene was kept in the solid phase rather than in the liquid solution, the latter being practically pure solvent. The samples prepared were stored in the hermetically sealed crucibles at room temperatures or at 260 K in the refrigerator for 1–3 days before measurements. Typically 3–5 samples of different compositions and pre-history 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. The most of the sealed pans were scanned several times. When solid solvates were found they were characterized by there temperature and enthalpies of the incongruent melting and by composition.

DSC was extensively used for examining of the solid-solid phase transitions [17], incongruent melting [1, 5, 7, 14] and even for direct determination of the formation enthalpies of the certain fullerene derivatives [18].

Temperatures of onsets of DSC peaks were used to indicate the incongruent melting temperatures of the solvates formed. DSC gave two reproducible estimations of the equilibrium incongruent melting temperature, namely, the onset temperature and the temperature of the peak maximum. It was mentioned, that the equilibrium incongruent melting temperature could be 5–15 degrees below the temperature of maximum [6], i.e. that onset temperatures, probably, gave better estimation. The final statement was proved in the additional DSC experiment with $Na_2SO_4\cdot10H_2O$, where measured onset temperature was close to the literature value, 305.7±0.5 K and 305.5 K, respectively. For the systems under study the onset temperatures were shown to be independent on the scanning rate in the DSC experiment. Further details of the DSC experimental procedure were already described [5]. This procedure allows one to prove the formation of the solid solvate in the system, to determine its temperature and enthalpy of the incongruent melting (decomposition). DSC of heterogeneous samples (solvate+saturated solution) became a method of choice for the determination of the composition of solvates. The compositions were calculated from the amount of fullerene and solvent that had been incorporated into a new solid structure. DSC peak, corresponding to the melting enthalpy of the solvent was measured in order to determine the amount of extra solvent that had melted and thus had not reacted. Fullerene was usually completely converted. The total amount of fullerene and solvent in the samples being known, the compositions of the solvates were estimated. Recalculation of solubility brings some order in the solubility date.

Results and discussion

DSC measurements showed the formation of solid solvates of C_{60} and C_{70} with the solvents in a number of systems studied. Formation of solvates was proved by disappearance of the smaller peaks (5–8 kJ per mole of fullerene) corresponding to solid-solid phase transitions in pure fullerene and by appearance of the new big peaks (13–50 kJ per mole of fullerene) corresponding to the incongruent melting transitions of solvates. The peak solid-solid phase transition on pure fullerene reappeared again after the solid solvate was destroyed by incongruent melting. In all cases the incongruent melting transitions took place below the boiling points of the solvents. In some of the systems more than one solvate was identified.

Compositions of the solvates formed along with the enthalpies and temperatures of their incongruent melting transitions are presented in Table 1.

This incongruent melting transitions correspond to the reactions

$$C_{60}n\mathrm{S}\ (s) = C_{60}m\mathrm{S}\ (s) + (n-m)\mathrm{S}\ (liq) \qquad (1)$$

or

$$C_{60}m\mathrm{S}\ (s) = C_{60}\ (s) + m\mathrm{S}\ (liq) \qquad (2)$$

here *S* is a solvent, *m* and *n* are stoichiometric coefficients.

Table 1 Thermochemical properties and compositions of the solvates of C_{60} and C_{70}

System	T_{imp}/K	ΔH_{imp}/kJ mol^{-1}	Solvate composition (molar ratio of C_{60} to solvent)
C_{60}–1,2–$C_6H_4Br_2$	350.9±1.1	40.1±1.9	2.9±0.1
C_{60}–1,3–$C_6H_4Br_2$	336.0±5.1 484.4±6.8	26.0±1.4 14.6±1.1	1.9±0.1 0.6±0.1
C_{60}–1,2,4–$C_6H_3Cl_3$	340.3±2.4	48.3±1.1	2.0±0.1
$C_{60}(N_2C_4H_8)$–1,2,4–$C_6H_3Cl_3$	397.9±2.3	13.8±0.3	1.0±0.1
C_{70}–1,3,5–$C_6H_3(CH_3)_3$	422.0±2.2	13.5±1.7	2.0±0.2

Table 2 Experimental (x) and re-calculated (x') solubility of C_{60}, C_{70}, $C_{60}(N_2C_4H_8)$

System	Ref.	$x(\text{exp})\cdot 10^4$	$x'(\text{hyp})\cdot 10^4$
C_{60}–C_6H_5Br	[5, 6]	4.4	48.8
C_{60}–1,2–$C_6H_4Br_2$	This study	23.1	265.0
C_{60}–1,3–$C_6H_4Br_2$	This study	23.1	730.9
C_{60}–C_6H_5Cl	[5, 6]	9.0	11.4
C_{60}–1,2–$C_6H_4Cl_2$	[5, 6]	38.3	67.6
C_{60}–1,2,4–$C_6H_3Cl_3$	This study	16.5	186.2
$C_{60}(N_2C_4H_8)$–1,2,4–$C_6H_3Cl_3$	This study	5.5	22.4
C_{70}–1,3,5–$C_6H_3(CH_3)_3$	This study	2.4	12.0
C_{60}–1,3,5–$C_6H_3(CH_3)_3$	[5, 6]	3.3	24.6
C_{60}–1,3–$C_6H_4(CH_3)_2$	[5, 6]	3.6	9.6
C_{60}–$C_6H_5(CH_3)$	[5, 6]	4.2	4.2

All of the solvates studied were relatively stable van der Waals complexes with the enthalpy of the reaction (1) or (2) per mole of a solvent being 13–40 kJ compared to the clathrates-type solvates of C_{60} with halogenated alkanes, alkenes, cycloalkanes, where the same enthalpy is equal to 0–3 kJ [19].

If one solvate was formed in the system, the reaction (2) only was observed. In case of two solvates, both reactions (1) and (2) were on the DSC trace (i.e. in the system C_{60}–1,3-$C_6H_4Br_2$).

Re-calculation of solubility

In order to compare solubility in different solvents, one has to be sure that they are saturated concentrations relative to one and the same solid phase, namely to solid C_{60}, C_{70} or fullerene derivative. Formation of solid solvates lowers the solubility relative to the case of 'hypothetical' pristine solid phase in equilibrium with the saturated solution. Simple thermodynamic considerations lead to the equation:

$$\ln(x'/x) = (\Delta H/R)(1/T - 1/T_{\text{imp}}) \tag{3}$$

here x' is 'hypothetical solubility' (molar fraction) relative to pristine, non-solvated solid phase and x is experimentally measured solubility (molar fraction), respectively. Both at $T=298$ K, ΔH and T_{imp} are the enthalpy and the temperature of the incongruent melting of the solvate, respectively, which is in equilibrium with the saturated solution at $T=298$ K. The values of x' are based on the onset temperatures, rather than on the temperatures of the peak maximum. When two solvates are formed in the system in order to calculate the 'hypothetical solubility' one has to use the equation:

$$\ln(x'/x) = \Delta H(1)/R(1/T - 1/T_{\text{imp}}(1)) + \\ + \Delta H(2)/R(1/T_{\text{imp}}(1) - 1/T_{\text{imp}}(2)) \tag{4}$$

here $\Delta H(1)$, $\Delta H(2)$ are two incongruent melting enthalpies and $T_{\text{imp}}(1)$, $T_{\text{imp}}(2)$ – two corresponding incongruent melting temperatures, $T_{\text{imp}}(2)>T_{\text{imp}}(1)$. The temperature dependence of both $\Delta H(1)$ and $\Delta H(2)$ was neglected. Since the saturated solution in equilibrium with the solid phases was very diluted in all cases, it was treated as a pure solvent.

In the recalculations of solubility it was assumed that the solid phase in equilibrium with the solution above the highest incongruent melting temperature found in the DSC experiment was a non-solvated fullerene or non-solvated fullerene derivative.

Experimentally measured and recalculated (hypothetical) solubilities of C_{60} at $T=298$ K in a number of solvents are listed in Table 2.

Conclusions

Though non-equilibrium solubility: x' 'relative to pristine C_{60}' cannot be observed in the experiment only these solubility which should be used in establishing correlation between solubility and other characteristics of the solution and in following 'relative to different solid phases' can hardly be compared. Only x' should be used in following the trends in solubility while going from solvent to solvent. It is worth noting that one need not know the composition of solvate in order to use the Eqs (3) and (4). As it is seen from the Table 2, recalculations of solubility brings some order into the solubility data. The recalculated values of solubility x' where the changes tend to reflect the efficiency of molecular interaction increase with increasing of number of methyl- and halogen- groups in the solvents molecules and also in the CH_3, Cl, Br for the series of solvents with the same type of substitution (column 4). The analogous tendency was revealed on the thermodynamic stability of solid solvates for the solvent series above in terms of standard Gibbs free energy of the reaction formation [5]. This trend is hardly seen with the measured solubility x (column 3).

For 1,2- and 1,3-dibrom-benzene where solubility x are equal, solubility 'hypothetical' x' are different. The tendency of 1,2-isomers to be better solvents for C_{60} compared to the 1,3-isomers was broken by the dibrom-benzenes, where x' is higher for 1,3-isomer. It can be speculated that the solubility of C_{60} may be sensitive to specific interactions caused by different structures of the isomeric solvent molecules.

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