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Binary systems of C_{60} with positional isomers 1,2- and 1,3-$C_6H_4Br_2$

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Abstract

Thermodynamic properties of binary systems of C_{60} with 1,2- and 1,3-dibromobenzenes have been studied by means of differential scanning calorimetry (DSC). Solid solvates with the compositions $C_{60}3(1,2\text{-}C_6H_4Br_2)$; $C_{60}2(1,3\text{-}C_6H_4Br_2)$ and $C_{60}0.6(1,3\text{-}C_6H_4Br_2)$ have been found. The solvates have been characterised by their enthalpies and temperatures of incongruent melting transition and in part by X-ray powder data. It has been shown that positional isomers 1,2- and 1,3- of the substituted benzenes formed two series of "typical" phase diagrams. Solubility behaviour of C_{60} in positional isomers has been discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: DSC; Fullerenes; Solvates; Solubility; Isomers

1. Introduction

The solubility of C_{60} and other fullerenes is of both practical and theoretical interest. The necessity of dissolving fullerenes in order to extract, purify and modify them chemically is obvious. Being a globular molecule, C_{60} is an excellent candidate for checking different models of solute–solvent interactions and solubility [1].

The thermodynamic studies of solubility behaviour of C_{60} in the most efficient aromatic solvents have shed light on the importance of studying solid solvate formation. The decomposition of these van der Waals complexes causes temperature maximums in solubility measurements [2].

Another intriguing feature of the solution behaviour of C_{60} is the large difference in solubility observed for positional isomers, e.g. for 1,2-dichlorobenzene, the room temperature solubility of C_{60} is about 10 times higher, than for 1,3-dichlorobenzene, 24.6 and 2.4 mg/ml, respectively [3]. The chemical properties and solvent parameters [4] of the two isomers are similar. It has been claimed [3], that differences in solubility in positional isomers can be due to the formation of solid solvates, different in structure and stability. The solubility is in part determined by the solid phase in equilibrium with the solution. In the case of C_{60} and aromatic solvents, this solid phase is usually a solid solvate (not pristine C_{60}!) with the geometry of the crystal lattice, controlled by the geometry/space structure of the solvent molecule, which is different in the case of two positional isomers. The effect of the solid phase combined with the similar properties of

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solvents themself can explain different solubilities in isomers. This idea, however, has not been proven experimentally. Even after using thermodynamic equations to account for the difference, caused by the formation of solvates, the solubility of C_{60} in 1,2- and 1,3-dimethyl- and dichlorobenzenes was still different [2].

This work focuses on the experimental study of the binary systems C_{60}–1,2- and 1,3-dibromobenzene. The solubilities of C_{60} in both solvents are *equal* according to [3]. The thermodynamics of solid solvates was studied by means of differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD). Phase diagrams of the binary systems of C_{60} with positional isomers and solubility behaviour of C_{60} in these solvents are discussed.

2. Experimental

Samples of C_{60} were obtained from Bucky, USA (99.5 mol% purity) and Fullerene Technologies, St. Petersburg, Russia (99 mol% purity). The solvents were commercial samples of 98% purity for 1,2-$C_6H_4Br_2$ and 97% for 1,3-$C_6H_4Br_2$ from Lancaster. A DSC-30 Mettler instrument was used to capture DSC traces. Measurements were taken at temperatures from 180 to 670 K with scanning rates 10 and 5 K/min (upscans and downscans). Several heterogeneous (solid–liquid) samples of the binary systems with molar ratios of fullerene to solvent less than 1:6.5 were treated. With such a ratio, more than 98% of the 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 hermetically sealed crucibles at room temperatures or at 260 K in a refrigerator for 1–3 days before measurements. Most of the pans were scanned several times. Temperatures of onset DSC peaks were used to indicate the transition temperatures [5].

Solvates of C_{60} lose their solvents easily. To prevent this loss, DSC offers a method to determine the composition of the solvate $C_{60}B$ (B = solvent) in the presence of an extra amount of solvent. This method is based on measuring of the amount of B in the sample that had not reacted to form the solvate. This amount of excess B was determined from the size of the solvent melting peak in DSC experiment. This excess solvent peak was then compared with the peak recorded for a known amount of pure solvent. The total amount of B in the sample was known from initial weighing. The extent of reaction of C_{60} in the sample could be followed through the order–disorder transition of C_{60} at 259 K. Solvate composition was determined only for samples where this peak had completely disappeared, indicating complete conversion of C_{60} to solvate.

Further details of the DSC experimental procedure have been described elsewhere [2]. This procedure allows one to prove the formation of the solid solvate in the system, to determine its enthalpy of the incongruent melting (decomposition) and its composition with the help of simple mass balance equations.

XRD data for solvated crystals were obtained at Siberian Synchrotron Radiation Centre (Novosibirsk) on a VEPP-3 storage ring.

3. Results and discussion

3.1. Thermodynamics

The formation of van der Waals type molecular complexes (solid solvates) were confirmed by means of DSC in both of the systems studied.

After the samples were maintained at room temperature for 1–3 days, the peak of the orientational phase transition at 260 K normally observed in the DSC of pristine C_{60} completely disappeared from the trace, while new endothermic peaks, corresponding to the incongruent melting of the solid solvates

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

$$C_{60}mS\,(\mathrm{s}) = C_{60}\,(\mathrm{s}) + mS\,(\mathrm{liq}) \qquad (2)$$

were found. Here, S is a solvent, and m and n are the stoichiometric coefficients. If one solvate was formed, only reaction (2) was observed. In the case of two solvates, both reactions (1) and (2) were on the trace. A peak, corresponding to melting of the "extra" solvent, which was present in the sample but was not incorporated into the solid solvate, was always seen as well.

The typical DSC traces of the binary systems with dibromobenzenes are presented in Figs. 1 and 2. One solvate was found in the system with

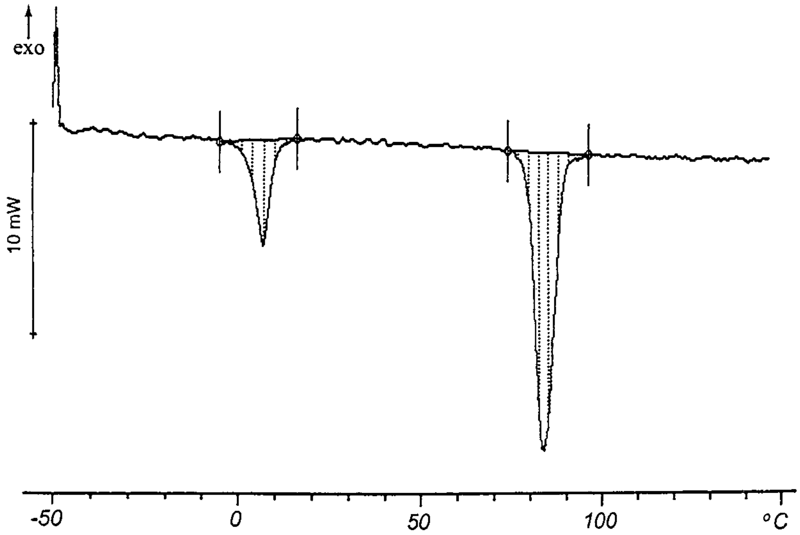

Fig. 1. DSC trace of the system C_{60}–1,2-dibromobenzene, heating rate 10 K/min.

1,2-dibromobenzene, while two solvates were formed with 1,3-dibromobenzene. The compositions (fullerene to solvent molar ratio) of the solvate with 1,2-dibromobenzene and of the "low temperature" solvate with 1,3-dibromobenzene were determined by means of a DSC technique utilising mass balance equations (see Section 2 and [2] for more details). These compositions were later confirmed by single crystal X-ray analysis [6]. They were found to be 1:3 with 1,2-dibromobenzene and 1:2 with 1,3-dibromobenzene. In addition, a second "high temperature" solvate was revealed in the system with 1,3-dibromobenzene. It was formed from the "low temperature" solvate at 336 K by reaction (1) and decomposed near the normal boiling point of solvent by reaction (2). In the case when two solvates were formed in the system, the

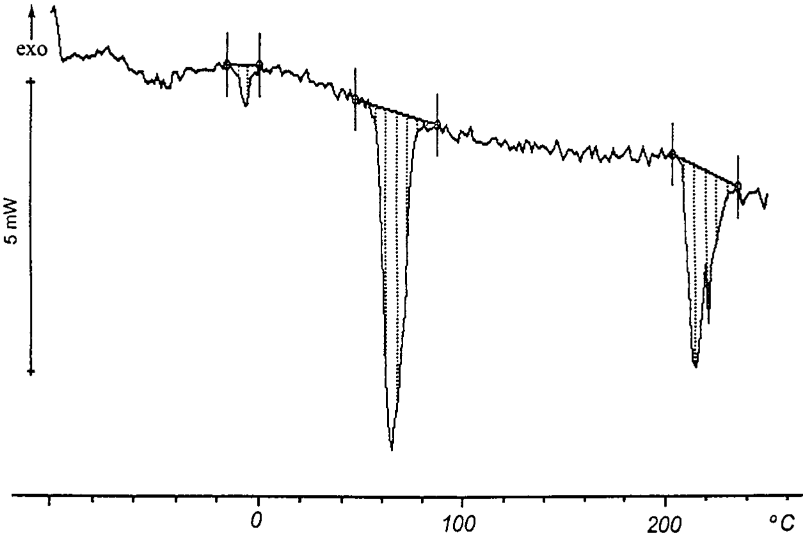

Fig. 2. DSC trace of the system C_{60}–1,3-dibromobenzene, heating rate 10 K/min.

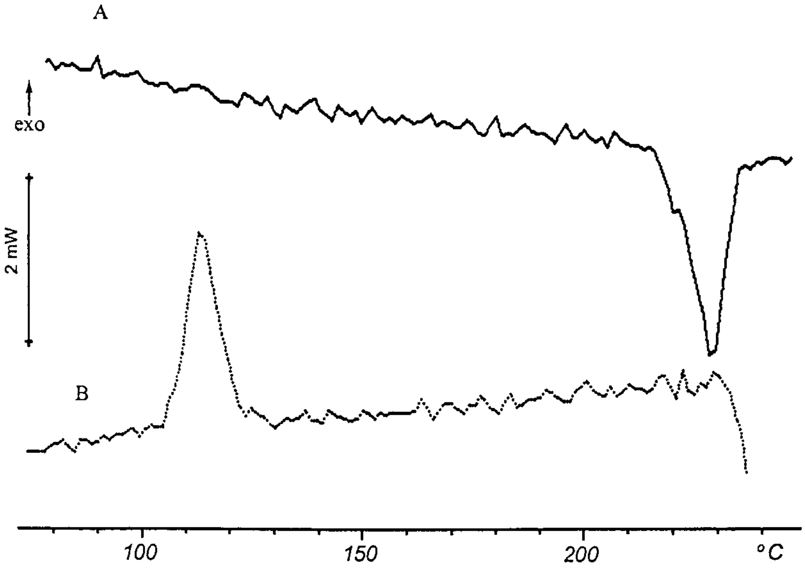

Fig. 3. DSC trace of the system C_{60}–1,3-dibromobenzene: (A) upscan, (B) downscan. Heating rate 10 K/min.

composition of the "high temperature" solvate was not directly determined, since the applied procedure [2] only allowed the determination of the composition of the "low temperature" solvate.

It is worthwhile to note that an exothermic effect was observed on the downscans with the samples of the system C_{60}–1,3-$C_6H_4Br_2$. Though at temperatures more than 100 K below the temperature of the incongruent melting (Fig. 3), the enthalpy of this effect only slightly differed from the enthalpy of decomposition of the "high temperature" solvate. The measured difference between the enthalpies of decomposition (reaction (2)) at the incongruent melting point and of formation (reaction, opposite of reaction (2)) at significantly lower temperature did not exceed 6%. It was concluded that the enthalpy of reaction (2) in this case was nearly temperature independent.

Enthalpies, temperatures of incongruent melting and DSC measured compositions of the solvates formed in the investigated binary systems are presented in the Table 1, along with the corresponding data from the literature [2,5] for the C_{60} solvates, formed by similar positional isomers. The entropies of decomposition deduced in the third column were

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

System	T (K)	ΔH (kJ/mol)	ΔS (J/mol K)	Solvate composition
C_{60}–1,2-$C_6H_4Br_2$	350.9 ± 1.1	40.1 ± 1.9	114 ± 6	2.9 ± 0.1
C_{60}–1,2-$C_6H_4Cl_2$, [2]	322[a], 342[b]	18.9 ± 1.5	59 ± 5[a], 55 ± 5[b]	2.0 ± 0.5
C_{60}–1,2-$C_6H_4Me_2$, [2,5]	310.3 ± 0.8	31.3 ± 1.4	101 ± 4	2.1 ± 0.2
C_{60}–1,3-$C_6H_4Br_2$	336.0 ± 5.1	26.0 ± 1.4	77 ± 6	1.9 ± 0.1
	484.4 ± 6.8	14.6 ± 1.1	30 ± 3	–
C_{60}–1,3-$C_6H_4Cl_2$, [2,5]	295.7 ± 1.6	28.5 ± 1.2	96 ± 6	2.1 ± 0.1
	394.5 ± 0.7	12.2 ± 0.5	31 ± 2	0.5 ± 0.2
C_{60}–1,3-$C_6H_4Me_2$, [2,5]	287.3 ± 1.6	24.3 ± 3.0	85 ± 8	2.3 ± 0.2
	362.4 ± 0.8	11.9 ± 0.7	33 ± 2	0.6 ± 0.1

[a] Freshly prepared sample.

[b] After storage, see [2].

Table 2
Gibbs free energies (reaction (2)) of the solvates of C_{60}

System	$\Delta_rG(2)$ (kJ/mol)	m (in reaction (2))
C_{60}–1,2-$C_6H_4Br_2$	6.0	3[c]
C_{60}–1,2-$C_6H_4Cl_2$	1.4[a], 2.4[b]	2[c]
C_{60}–1,2-$C_6H_4Me_2$	1.2	2[c]
C_{60}–1,3-$C_6H_4Br_2$	8.6	2[c]
C_{60}–1,3-$C_6H_4Cl_2$	2.8	2
C_{60}–1,3-$C_6H_4Me_2$	1.2	2
C_{60}–1,3-$C_6H_4Br_2$	5.6	0.5–0.6
C_{60}–1,3-$C_6H_4Cl_2$	3.0	0.5[c]
C_{60}–1,3-$C_6H_4Me_2$	2.1	0.6[c]

[a] Freshly prepared sample.

[b] After storage, see [2].

[c] Solid solvates in equilibrium with the saturated liquid solution at $T = 298$ K.

calculated as changes of entropies for the phase reactions $\Delta_rS = \Delta_rH/T$. With the 1,3-isomers, two solvates were present in the system, the first line of Table 1 corresponds to reaction (1), while the second to reaction (2).

Table 2 summarises the standard Gibbs free energies of reaction (2) for the solid solvates of C_{60} at $T = 298$ K. These values were calculated from the enthalpies and the entropies in Table 1, assuming that both of the latter were temperature independent. The thermodynamic stability of the solvates of C_{60} increased for the both 1,2- and 1,3-isomers in the line CH_3–Cl–Br.

3.2. Solid solvates with the composition $C_{60}(0.5–0.6)S$

In the systems of C_{60} with 1,3-isomers, the solvated crystals with the composition 1:(0.5–0.6) were observed. XRD patterns showed a striking similarity to the unit cell parameters for these solvates (Table 3). All the solvates belonged to the hexagonal lattice type. In this case, stereochemical similarity of the solvent molecules led to the formation of the isomorphic solvates.

Table 4
Experimental and recalculated solubilities of C_{60} in 1,2- and 1,3-$C_6H_4X_2$

System	Reference	x (exp) ($\times 10^4$)	x (hyp) ($\times 10^4$)
C_{60}–1,2-$C_6H_4Br_2$	This study	23.1	265.0
C_{60}–1,2-$C_6H_4Cl_2$	[2,5]	38.3	67.6
C_{60}–1,2-$C_6H_4Me_2$	[2,5]	14.7	24.0
C_{60}–1,3-$C_6H_4Br_2$	This study	23.1	730.9
C_{60}–1,3-$C_6H_4Cl_2$	[2,5]	3.8	12.7
C_{60}–1,3-$C_6H_4Me_2$	[2,5]	3.6	9.6

Similarity in the crystal structures led to similar values of the reaction entropies. As seen from Table 1, the entropies of reaction (2) for the solvates under discussion are almost equal (30–33 J/mol K). Similar solvate was found in the system of C_{60} with 1,3,5-trimethylbenzene with the entropy of reaction (2) equal to 33–38 J/mol K [2].

"High temperature" solvate, formed in the system of C_{60}–1,3-$C_6H_4Br_2$ belongs to this group. Based on the data, presented in Tables 1 and 4, it was assumed that it has 1:0.6 composition.

3.3. "Typical" phase diagrams

Figs. 4 and 5 present "typical" phase diagrams for the binary systems of C_{60} with 1,2- and 1,3-substituted benzenes, respectively. In all of the systems with 1,2-isomers (1,2,4-trimethylbenzene also belonging to this group) one solvate with the composition 1:2 or 1:3 was

Table 3
Parameters of elementary cell of the C_{60} solvates

Crystalline	Lattice	a	c	V	Z	k[a]
$C_{60}y$(1,3-$C_6H_4Br_2$)[c]	Hexagon	23.86(3)	10.11(1)	4984	6	0.71[b]
C_{60}0.6(1,3-$C_6H_4Cl_2$)	Hexagon	23.8098(9)	10.130(1)	4973	6	0.70
C_{60}0.6(1,3-$C_6H_4Me_2$)	Hexagon	23.786(7)	10.15(2)	4973	6	0.72
C_{60}0.5(1,3,5-$C_6H_3Me_3$)	Hexagon	23.742(1)	10.167(1)	4963	6	0.71

[a] Coefficient of packing $k = ZV_{\mathrm{vdw}}/V_{\mathrm{cell}}$.

[b] Calculated at $y = 0.6$.

[c] In the case of high-temperature solvate of C_{60} with 1,3-dibromobenzene, powder diffraction pattern obtained was poor resolved due to the large widths of peaks and one of 16 lines observed was unindexed.

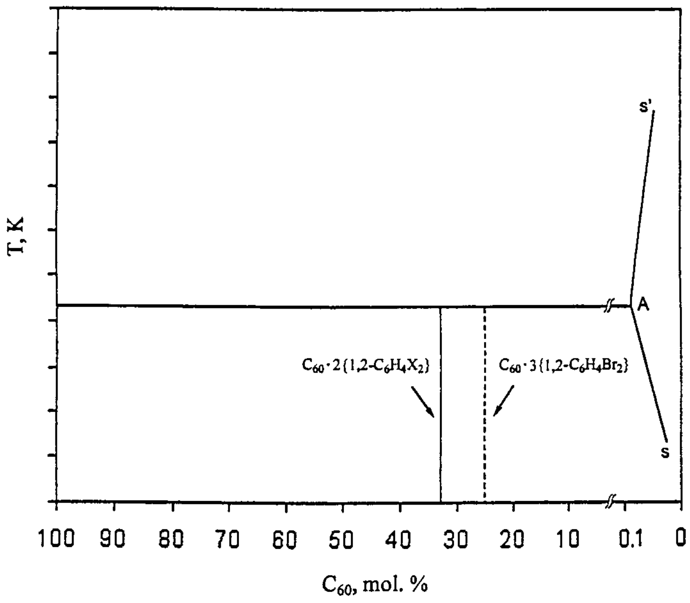

Fig. 4. "Typical" phase diagram for the binary systems of C_{60} with 1,2-substituted benzenes.

found. This solvate undergoes incongruent melting (reaction (2)) with the incongruent melting temperature being temperature of maximum solubility of C_{60} (point A in Fig. 4). Such a maximum was experimentally observed in the system with 1,2-dimethyl- and 1,2-dichlorobenzene [7,8]. The same maximum can be predicted in the systems with 1,2-dibromobenzene and 1,2,4-trimethylbenzene.

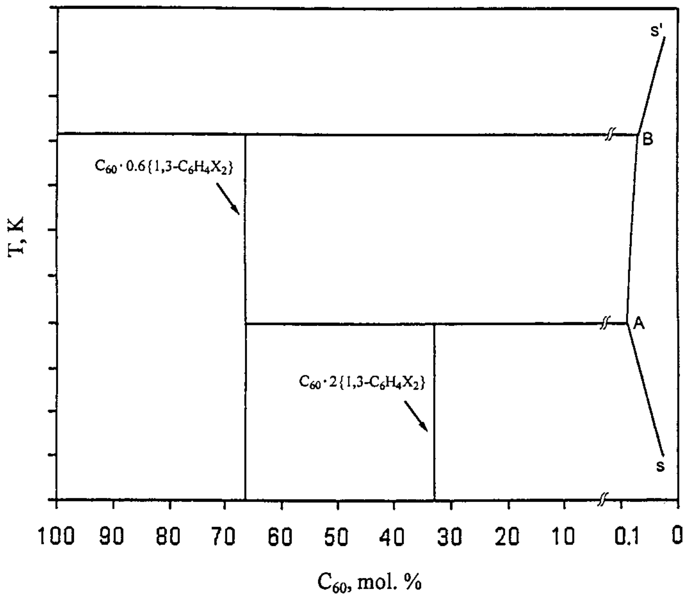

Fig. 5. "Typical" phase diagram for the binary systems of C_{60} with 1,3-substituted benzenes.

The 1,3-isomers (including 1,3,5-trimethylbenzene) form the second group with the phase diagram, presented in Fig. 5. Here, two solvates with the composition 1:2 and 1:(0.5–0.6) were formed. Two incongruent melting points, corresponding to reactions (1) and (2) were observed. Crystal structures of 1:(0.5–0.6) solvates are similar. Line SABS' in Fig. 5 schematically presents the saturated concentrations of C_{60} in the liquid solution. The shape of the line can be calculated only in the case of 1,3-dichlorobenzene from the data of [2]. Solubility of C_{60} in 1,3-dichlorobenzene has to reach maximum at point A, and has to be almost temperature independent between points A and B. The latter is due to the fact that the enthalpy of dissolution in 1,3-dichlorobenzene (−12 kJ/mol) [2] is practically equal to the enthalpy with the opposite sign of reaction (2) (12 kJ/mol) (see Table 1).

The similarity of the phase diagrams of the binary systems of C_{60} with the same type of positional isomers confirms that the shape of the solvent (guest) molecule plays a significant role in the structure/stability of the C_{60} solvates. Transition from the 1,2- to 1,3-isomer results in a new type of a phase diagram.

Another "typical" phase diagram was reported for the systems of C_{60} with the small globular molecules CCl_4 and C_6H_{12} [9].

3.4. Solubility behaviour

Experimentally measured room temperature solubilities of C_{60} in positional isomers, x, are presented in Table 4 (column 3). As seen from the table, solubilities within the pair of 1,2- and 1,3- similar solvents are significantly different. A possible explanation may be the formation of different solid solvates from different isomers at room temperature. To compare the efficiency of solvents, one needs to compare solubilities relative to one and the same solid phase, namely pristine C_{60}, in different systems. Instead of measured solubilities in molar fractions, x, "hypothetical", relative to C_{60} solubilities, x', have to be compared. Hypothetical solubilities can be easily calculated with the help of the equation [2]

$$x' = x \exp\left(\frac{\Delta_r G(2)}{RT}\right) \qquad (3)$$

with $\Delta_r G(2)$ from the Table 2. Gibbs free energies $\Delta_r G(2)$ of the solid solvates which are in equilibrium with the saturated liquid solution at $T = 298$ K were used.

Solubilities x' are listed in Table 4 (column 3). As seen from the Table, recalculation did not bring any improvement. Solubilities x' for positional isomers are still different. For 1,2- and 1,3-dibromobenzene where solubilities x are *equal*, solubilities 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 dibromobenzenes, where x' is higher for 1,3-isomer.

In the case of 1,2- and 1,3-dichlorobenzene, the enthalpies of dissolution of C_{60} were measured [2]. Based on these data, it can be stated that the difference in solubility of C_{60} (x') between the 1,2- and 1,3-isomers (factor 5.2) is due to both the more negative partial enthalpy of dissolution (factor 1.8) and the less negative partial entropy of dissolution (factor 2.9) in 1,2-diclorobenzene.

Liner regression analysis with respect to relevant solvent parameters [4,5] has predicted close solubilities (30% difference at most) of C_{60} in 1,2- and 1,3-isomers of dimethyl and dichlorobenzene. Other approaches recently used to explain the trends in solubility of C_{60} [10,11] do not deal with the solubility of the isomers.

Byrne et al. [12] have studied the solubility of noble gases, CO_2, CH_4, CF_4, SF_6 in 1,2-, 1,3- and 1,4-dimethylbenzene. The authors [12] have found the solubilities in different isomers to be almost equal (10% difference at most) in good accord with the predictions of the scaled particle theory (SPT) [13].

Solubility of C_{60} in aromatic solvents may be called "interactive", since it is featured by significant negative partial enthalpies of solution (−(12–20) kJ/mol) and negative partial entropies of solution (−(90–100) J/mol K), compared to SF_6, CF_4, etc. [2]. Ideal, regular, SPT models based on weak solute–solvent interactions, do not seem to work for fullerenes. It can be speculated that being "interactive", the solubility of C_{60} may be sensitive to specific interactions, caused by different structures of the isomeric solvent molecules.

Acknowledgements

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