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C60·Bromobenzene Solvate: Crystallographic and Thermochemical Studies and Their Relationship to C60 Solubility in Bromobenzene

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Differential scanning calorimetry, solution calorimetry, and room-temperature single-crystal X-ray diffraction were used to study the thermodynamic and structural properties of a solvated crystal $C_{60} \cdot 2C_6H_5Br$. In the monoclinic solvate, two orientations of C_{60} were observed with fractional populations of 0.71 and 0.29. The enthalpy of solution of pure C_{60} in bromobenzene was determined to be $\Delta_{sol}H[C_{60}(s)] = -11.5 \pm 2.0$ kJ/mol. The enthalpy of solution of the solvated crystal was $\Delta_{sol}H[C_{60} \cdot 2C_6H_5Br(s)] = +28 \pm 1$ kJ/mol. The phase diagram of the system $C_{60}-C_6H_5Br$ for $T < 423$ K was constructed. It predicts the existence of a maximum in the temperature−solubility relationship for C_{60} in bromobenzene at 350 K. The activity of bromobenzene vapor over the solvated crystal is predicted to be reduced from its value over the pure liquid by a factor of 3.5.

Introduction

Aromatic solvents are of particular importance in fullerene chemistry. Because C_{60} has a relatively large solubility in solvents such as 1,2-dichlorobenzene, aromatic solvents are widely used in the extraction and purification of fullerenes and as media for organic functionalization reactions. Crystalline solvates of fullerenes have been extensively studied in recent years. Among the properties investigated were thermal stability, crystal structure, and the motion and disorder of molecular units in the solid.[1−5] As has been recently shown, the tendency of C_{60} to form solvates with aromatic solvents, combined with the tendency of the pure solid to dissolve exothermically in solvents, greatly influences fullerene dissolution.[6−9] The formation and incongruent melting of C_{60} crystals solvated with aromatic solvents causes solubility maxima and discontinuous changes of the slopes of solubility versus temperature curves.

The temperature dependence of the solubility of fullerenes in a solvent Y is described by the following equations. Below the incongruent melting point T_{imp}, the equilibrium between solid and saturated solution, expressed in terms of chemical potential, is

$$\mu[C_{60} \cdot nY(s)] = \mu[C_{60}(satd)] + n\mu[Y(liq)] \quad (1)$$

and the temperature dependence of solubility is given by

$$d \ln x(C_{60})/dT = \{\Delta_{sol}H[C_{60}(s)] - \Delta_r H[C_{60} \cdot nY(s)]\}/RT^2 \quad (2)$$

Above T_{imp}, the equilibrium is

$$\mu[C_{60}(s)] = \mu[C_{60}(satd)] \quad (3)$$

$$d \ln x(C_{60})/dT = \Delta_{soln}H[C_{60}(s)]/RT^2 \quad (4)$$

Here x is the mole fraction of fullerene in the saturated solution, $\Delta_{soln}H[C_{60}(s)]$ is the enthalpy of dissolution of C_{60} into saturated solution, n is the number of solvent Y molecules, and $\Delta_r H[C_{60} \cdot nY(s)]$ the enthalpy of the reaction of C_{60} that leads to the formation of a solid solvate:

$$C_{60}(s) + nY(liq) = C_{60} \cdot nY(s) \quad (5)$$
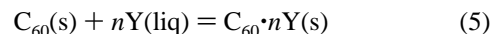
The maximum of solubility is caused by the unusual relation between the enthalpies in eqs 2 and 4. The enthalpies of dissolution of C_{60} in aromatic solvents are negative. If the enthalpy of reaction 5 is more exothermic than the enthalpy of dissolution of C_{60}, the temperature dependence of solubility below T_{imp} is positive. The model starts from strictly thermodynamic equations that contain no assumptions about the molecular nature of pure or solvated crystals other than their composition. The solutions are dilute, so mole fractions are used in eqs 2 and 4 instead of activities, and $\Delta_{soln}H$ is assumed to equal the partial molar enthalpy of solution.

Temperature maxima of solubility, brought about by the incongruent melting of solvated crystals, the reverse of reaction 5, have been found in the systems C_{60}/toluene and C_{60}/o-xylene.[6−9] In both cases the solvated crystal has the composition $C_{60} \cdot 2Y$. In this paper we show by room-temperature single-crystal X-ray diffraction that the solvate of C_{60} with bromo-

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benzene has the same composition, and we use differential scanning calorimetry (DSC) and solution calorimetry to investigate the incongruent melting of the solvate and the thermodynamics of the solubility of C$_{60}$ in bromobenzene.

Experimental Section

Samples of C$_{60}$ (doubly sublimed, 99.99% mol purity, MER Inc.) were used without further treatment. Bromobenzene with the trademark HP was distilled twice before use (Moscow); in Lund, reagent grade (Fluka, 99.5% by GC) was used without further purification.

X-ray Crystallography. Single crystals of a solvate suitable for diffraction study were obtained from the saturated solution of C$_{60}$ in bromobenzene by slow evaporation at room temperature (5 days). Rhombohedral crystals were produced. A single crystal was transferred directly from the mother liquor to an inert oil and mounted on a glass fiber in a diffractometer.

Single-crystal X-ray diffraction data were collected at room temperature on a Siemens P3 diffractometer in the Center for X-ray Studies of the Institute of Organoelement Compounds (Mo Kα radiation, graphite monochromator, $\lambda = 0.7107$, $\mu = 22.1$ cm^{-1}, absorption correction not applied). A total of 2497 reflections with $4 < 2\theta < 56°$ were collected. The structure was solved by direct methods using SHELXS-86 and refined using SHELXL-93 with anisotropic thermal parameters for non-hydrogen atoms in C$_6$H$_5$Br and for coinciding C atomic positions in the C$_{60}$ moiety (vide infra).

A difference Fourier map revealed a rotational disorder due to a second orientation of the C$_{60}$ molecule. The occupancies of two orientations (A and B) of C$_{60}$ were refined with a constraint $g(A) + g(B) = 1$ to the values of $g(A) = 0.71$ and $g(B) = 0.29$; carbon atoms of both orientations with the separate positions (i.e., "crosses") were refined isotropically. Hydrogen atoms in the C$_6$H$_5$Br molecule, located in a difference Fourier map, were included into a refinement in calculated positions using a Riding model. Finally $R = 0.057$, $R_w = 0.154$ for 2206 reflections with $I > 2\sigma I$ and $R = 0.094$, $R_w = 0.189$ for all 2417 reflections. The residual electron density map contains a number of peaks lower than 0.96 e/Å^3; most of these peaks were located on the surface of the C$_{60}$ molecule. Together with the broad range of C−C distances in C$_{60}$, these peaks probably point to an additional disorder of the fullerene moiety, which was not analyzed further. The absolute configuration was determined by the value of Flack parameter. The stoichiometry of the solvate was determined to be C$_{60}$·2C$_6$H$_5$Br; thus, in eqs 1, 2, and 5, $n = 2$.

Crystal data: C$_{72}$H$_{10}$Br$_2$, $M = 1034.68$, monoclinic, space group $C2$, $a = 17.231(4)$, $b = 10.164(3)$, $c = 11.338(3)$ Å, $a = 108.12(3)°$, $V = 1887(1)$ cm^3, $Z = 2$, $D_c = 1.821$, $F(000) = 1024.0$. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

Differential Scanning Calorimetry. A Mettler DSC-30 at Moscow State University was used to obtain the DSC curves. The melting points of pure solvents were used for temperature calibration. Measurements were taken at temperatures from 200 to 390 K at scanning rates of 5 or 10 K/min. It was observed that measured temperatures of the incongruent melting depended upon the scanning rates. Extrapolation to zero rate lowered temperatures of T_{imp} by 5−10 K. These extrapolated values were believed to correspond to the real temperature of equilibrium transition. The same conclusions were reached by Nagano and Tamura.[5] Temperatures of maxima of DSC peaks are used

to indicate the transition temperatures. Exo- or endothermic enthalpies of transitions were independent of the scanning rate.

Heterogeneous (solid/liquid) samples with different mole ratios of C$_{60}$ to bromobenzene were prepared in sealed DSC pans. The mole ratio of solvent to fullerene was chosen in such a way that more than 98% of fullerenes were kept in the solid phase rather than in the saturated liquid solution, thus ensuring that the latter contributes negligibly to the DSC scans. Before each measurement, samples were left to stand at room temperature or at $T = 261$ K in the refrigerator for a period of time from 1 to 5 days. Each sample was scanned several times. Data for the samples with different prehistories were identical, which proves that the equilibrium phase composition was reached. Further details of the DSC experimental procedure have been described elsewhere.[6,8,9]

Solution Calorimetry. An isothermal, heat conduction microcalorimeter,[10] recently designed and constructed at Lund University, has been used in these measurements. Solid C$_{60}$ samples of 1.5−7 mg were weighed (±0.005 mg) into stainless steel sample cups of ca. 40 μL volume, stored in the lid of the solvent ampule, and separated from the solvent vapor by a Kalrez O-ring. After overnight thermal equilibration within the calorimeter, they are introduced sequentially into an ampule containing 18 mL of solvent, and the heat flow dQ/dt for each insertion is measured as a function of time for several hours or until the signal returns to its baseline. A constant-temperature bath (TAM, Thermometrics AB) controls the environment of the microcalorimeter such that the baseline is stable to better than ±1 μW over the 8-h period of measurement. The heat evolved or absorbed for a given experiment is obtained by time integration of the heat-flow signal. A correction to this signal is made for the effect of introducing an empty sample cup into the solvent ampule. These corrections are usually 1−3 mJ, and analysis of their dQ/dt vs time traces shows that the corrections are caused by both endothermic (solvent evaporation) and exothermic (friction of O-ring seals) effects.

Results

X-ray Crystallography. The crystal structure of the molecular complex C$_{60}$·2C$_6$H$_5$Br (**I**) contains C$_{60}$ molecules in positions on the 2-fold axes and bromobenzene molecules in general positions. Despite the rotational disorder of the C$_{60}$ moiety that reduce the precision of the crystal structure (vide supra), geometrical parameters of bromobenzene molecule and average C−C bond lengths in C$_{60}$ molecules have their normal values. C$_{60}$ molecules form hexagonal close-packed layers in the *ab* plane with C$_6$H$_5$Br molecules placed in the interlayer space in the voids between fullerene spheres (Figure 1a,b). A general motif of the layered crystal structure of I corresponds to a slightly distorted primitive hexagonal packing of C$_{60}$ molecules with C$_6$H$_5$Br molecules in the cavities. A similar type of hexagonal layered packing was observed earlier in a series of C$_{60}$·2D complexes, where D = ferrocene,[11] P$_4$,[12] or small donor molecules.[13] The shortest distances between the centers of C$_{60}$ spheres in **I** are 10.00−10.16 Å within a layer and 11.34 Å between the layers. Molecules of C$_{60}$ are rotationally disordered in the same manner as found earlier in X-ray diffraction studies of two other complexes of C$_{60}$.[14,15] Two orientations of the C$_{60}$ moiety (A and B) are linked with a rotation by 180° about the line crossing the centers of two opposite 6−5 bonds in the molecule. However, unlike the above two structures,[14,15] the A and B orientations are unequally occupied in **I**, the ratio of their occupancy factors is close to 0.7:0.3. For 24 symmetrically independent carbon atoms in C$_{60}$,

a

b
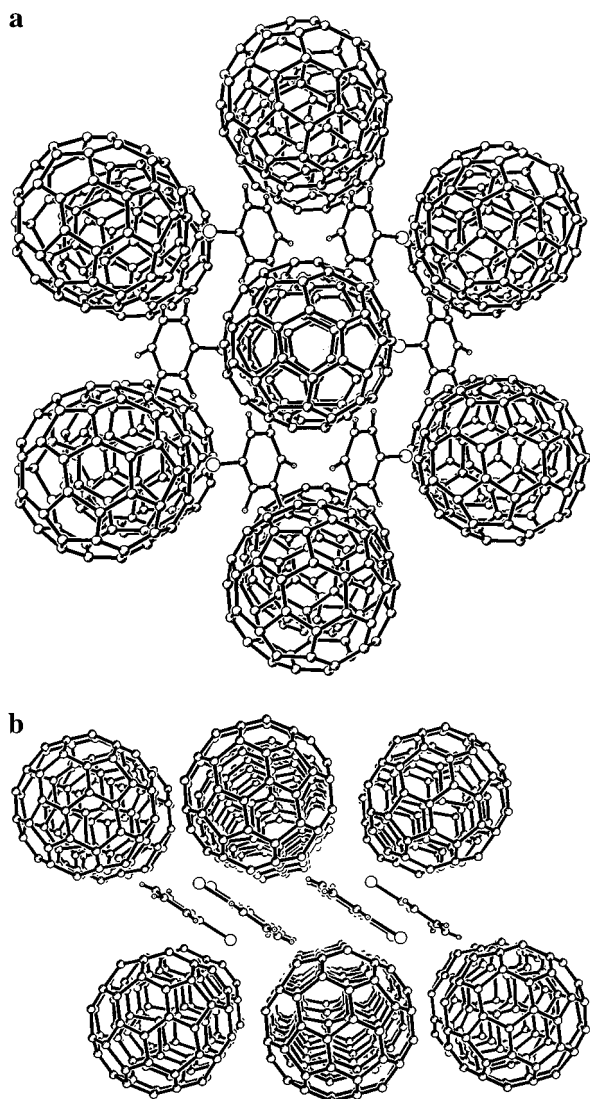

Figure 1. Crystal structure of $C60 \cdot 2C_6H_5Br$ (**I**): (a, top) As viewed perpendicular to the layers. Only one orientation of C_{60} molecules is shown, called "A" in the text, with the occupancy factor of 0.71. (b, bottom) As viewed along the layers. Orientation A of C_{60}.

the positions in both orientations are very close to each other; in the refinement of **I** these positions were approximated by one C atom. Partially occupied positions that are well separated in space form characteristic "crosses" in octahedral sites over the fullerene sphere (see also refs 14 and 15).

Each C_{60} molecule is surrounded by 6+2 fullerene neighbors and 12 C_6H_5Br molecules. Each brombenzene molecule points its C−Br bond toward the center of the hexagonal face of one neighboring C_{60} molecule (in A orientation) and is stacked over the "cross" of partially occupied atomic positions of another C_{60} neighbor (Figure 2). The shortest intermolecular contacts for C_6H_5Br in **I** are 3.64−3.92 Å (Br···C) and 3.40−3.68 Å (C···C); corresponding sums of the van der Waals radii are 3.65 and 3.40 Å, respectively[15]). Two types of the interlayer C_{60}−C_{60} stacking, also close to sums of van der Waals radii, are observed in **I**: "hexagon-to-hexagon" and "hexagon-to-cross". It is noteworthy that the higher populated (A) orientation of C_{60} molecules has shorter nonbonded contacts in the crystal than the less populated (B) orientation.

The structure of **I** reveals an absence of any specific intermolecular interaction stronger than the normal van der Waals forces. Solvate **I** is therefore a normal molecular complex
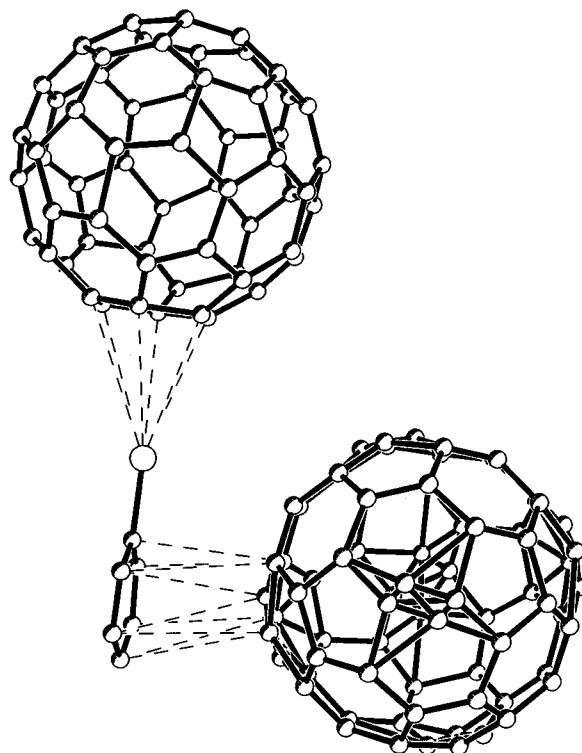

Figure 2. van der Waals contacts of bromobenzene molecule with the two closest C_{60} molecules. Only the major (A) orientation is shown in the right C_{60} molecule, while for the second molecule both orientations (A and B) are shown. Hydrogen atoms are omitted for clarity.
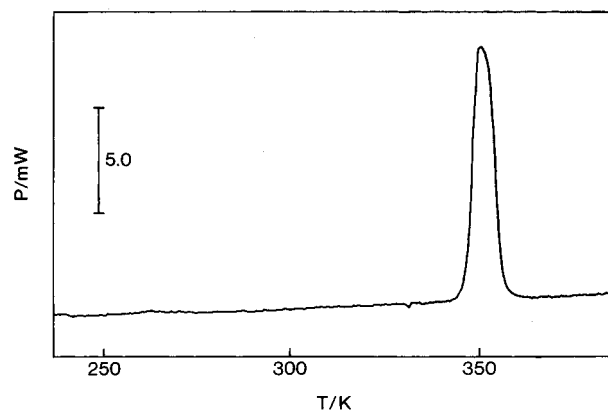
Figure 3. DSC scan of a heterogeneous sample of C_{60}−liquid bromobenzene after 24 h at room temperature.

with only a small extent of charge transfer between the molecular components.

Differential Scanning Calorimetry. Three heterogeneous (solid/liquid) samples with mole ratio of C_{60} to bromobenzene 1:13.6 (1), 1:6.8 (2), and 1:5.4 (3) were studied. After the samples had been maintained at room temperature for 1 day, the peak of the orientational phase transition at 259 K normally observed in the DSC of pristine C_{60} has completely disappeared from the curve, while a sharp, well-shaped endothermic peak at 350 ± 1 K with an enthalpy of 42 ± 2 kJ/mol (mean value for seven measurements) is found. A typical DSC curve is shown in Figure 3. This enthalpy change is due to the incongruent melting of a solvate of C_{60} with bromobenzene, the reverse of reaction 5. A broad exothermic peak arising from the formation of the solvate was observed in the DSC curve while scanning down from 370 to 220 K. The corresponding enthalpy was close to −42 kJ/mol.

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a

b
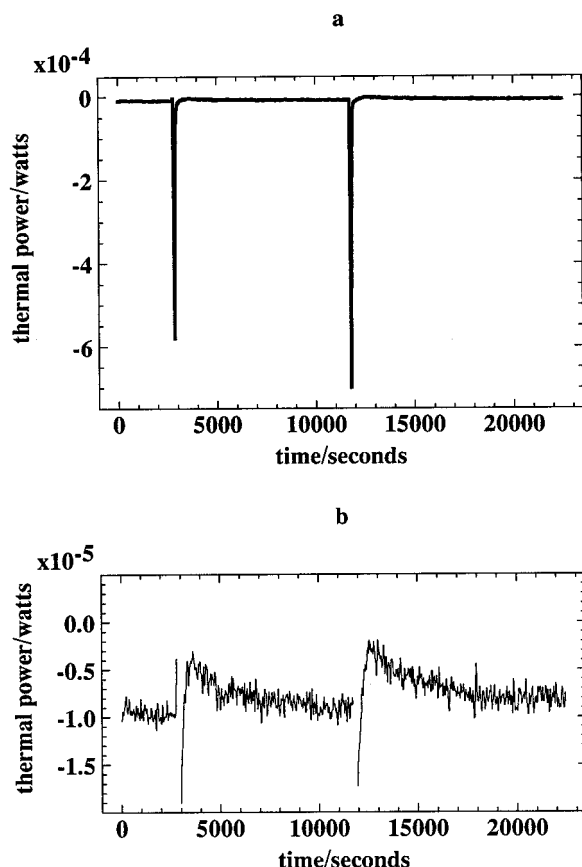
Figure 4. Isothermal heat conduction calorimetry signal from the dissolution of 1.97 and 2.11 mg of C$_{60}$ in bromobenzene at 298 K. This signal has been corrected for the time constant of the calorimeter using Tian's equation (see text). Figure 4b is an expanded-scale version of the base of the peaks in Figure 4a.

Crystals of C$_{60}$ solvated with bromobenzene were grown by precipitation from the solution. The solution was concentrated by careful evaporation at 330 K. The crystals were then collected on a glass filter and dried in air at room temperature. DSC scan with the dry sample showed the same endothermic peak at 350 K with the same enthalpy as with heterogeneous mixtures.

The solvate composition was determined with the help of DSC in two ways. First, DSC scans of the mixtures of solid C$_{60}$ and bromobenzene (with the initial composition accurately measured) were carried out after the solvate was formed. The amount of nonbound bromobenzene was determined from measurements of the peaks arising from the freezing or melting of the excess solvent in the DSC scans. Five measurements with the samples 2 and 3 gave the composition 1:(2 ± 0.2). This ratio of C$_{60}$ to bromobenzene was confirmed in experiments with the dry solvate, where composition was determined from the weight loss of a sample after complete removal of bromobenzene at 525 K.

Solution Calorimetry. When samples of 1.97 and 2.11 mg of C$_{60}$ were introduced into bromobenzene, unusual thermal power vs time traces were observed. Figure 4 shows these signals, corrected for the 200 s time constant of the calorimeter by means of Tian's equation.[16] A fast exothermic process, complete in a few minutes, was followed by a slower endothermic process lasting almost 2 h. Notice also in Figure 4 that the baseline is slanting upward, indicating a very slow endothermic process not completed during the experiment. When the calorimeter vessel was opened, undissolved solid material remained, which dissolved in excess bromobenzene.

From spectrophotometry of two solutions it was determined that 0.75 mg of the original 4.08 mg remained undissolved at the end of the experiments.

We interpret these data as evidence for two simultaneous exothermic processes occurring initially: dissolution of solid C$_{60}$ and formation of the solid solvate, C$_{60}$·2C$_6$H$_5$Br. Note that reaction 5 represents a strongly exothermic process (in the present case $\Delta H = -42$ kJ/mol). These fast exothermic processes were followed by a very slow endothermic dissolution of the remaining solvate, which did not dissolve completely before the experiment ended. By assuming that n' moles of the initial n moles of C$_{60}$ present (both samples) formed solvate (and the rest dissolved), the integrated thermal power traces can be analyzed to determine $\Delta_{soln}H[C_{60}(s)]$ if a value of $\Delta_{soln}H[C_{60}·2C_6H_5Br(s)]$ is calculated from the known enthalpy of decomposition. For this run only, the exothermic contributions of dissolution of C$_{60}$ and formation of the solvate were comparable in size, but for the two other runs conducted the dominant contribution to the thermal signal was dissolution of C$_{60}$ because of different compositions. Averaging the results of three runs gives $\Delta_{soln}H[C_{60}(s)] = -11.5 \pm 2.0$ kJ/mol.

Solvated crystals of C$_{60}$ were prepared from bromobenzene. Samples of this solvate dissolved endothermically in bromobenzene. The average of two experiments with ∼3 mg samples gives $\Delta_{soln}H[C_{60}·2C_6H_5Br(s)] = +28 \pm 1$ kJ/mol.

Using the two enthalpies of solution to compute the enthalpy of formation of the bromobenzene solvate (reaction 5) we get $\Delta H_f(C_{60}·2C_6H_5Br(s)) = -39.5 \pm 3.0$ kJ/mol. To within experimental error this agrees with the value of -42 kJ/mol determined from DSC.

Discussion

The thermodynamic data presented here can be used to calculate the ratio of the bromobenzene activities, or partial pressures, over the solvate and the pure solvent at 298 K. At the incongruent melting point of the solvate (350 K), $\Delta G_5 = \Delta H_5 - T\Delta S_5 = 0$ for the formation of the solvate (reaction 5). Using $\Delta H_5 = -42$ kJ/mol gives $\Delta S_5 = -120$ J/(K mol). Assuming that both ΔH_5 and ΔS_5 are independent of T, the Gibbs energy change ΔG_5 at 298 K is -6.2 kJ/mol for the reaction C$_{60}$(s) + 2B(l) = C$_{60}$·2B(s), where B represents bromobenzene. Note that the negative Gibbs energy change implies spontaneous formation of the solvated crystal from its components. To estimate P_B, the equilibrium partial pressure of bromobenzene over the solvate, consider the reaction

$$C_{60}·2B(s) = C_{60}(s) + 2B(g) \qquad (6)$$
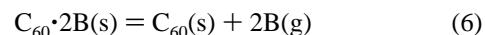
for which

$$\Delta G_6° = -RT \ln P_B{}^2 \qquad (7)$$

For the liquid−vapor equilibrium of bromobenzene at 298 K we have

$$B(l) = B(g) \qquad (8)$$

$$\Delta G_8° = -RT \ln P_B{}^* \qquad (9)$$

where P_B^* is the vapor pressure of pure liquid bromobenzene. Since the combination of reactions [5] + [6] − 2[8] is the null reaction, $\Delta G_5 + \Delta G_6° - 2\Delta G_8° = 0$, which yields $P_B/P_B^* = 0.28$. Thus, the activity of bromobenzene vapor over the solvated crystal is reduced from its value over the pure liquid by a factor of 3.5.
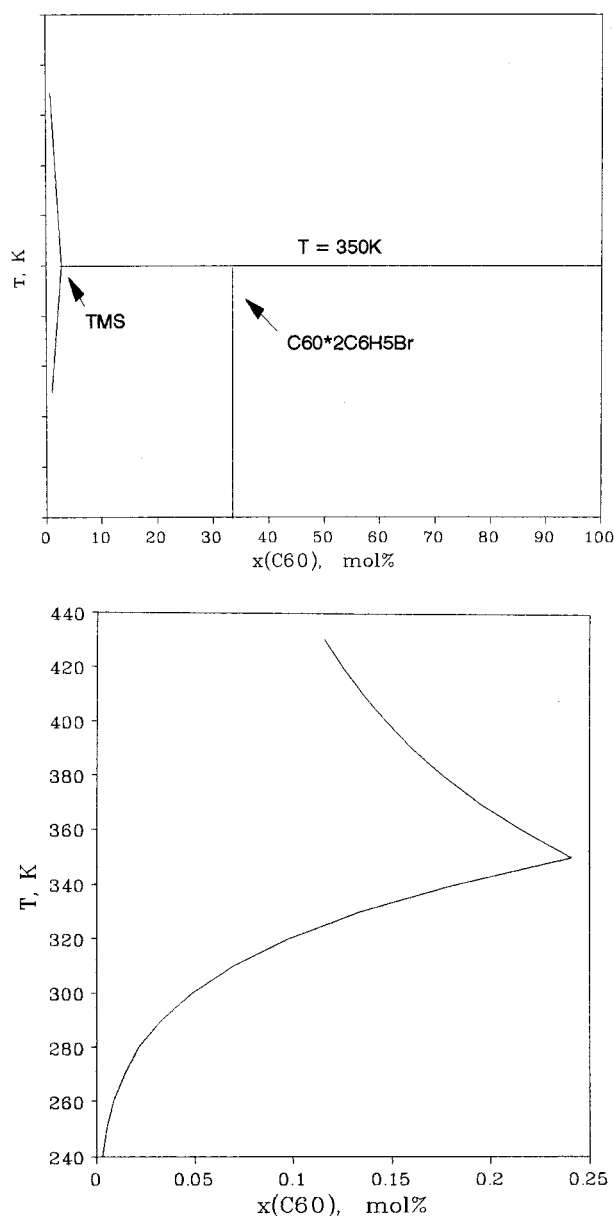
Figure 5. Phase diagram of the system C_{60}-bromobenzene: (a, top) general view; (b, bottom) part of the diagram, close to pure bromobenzene showing the temperature vs solubility curve.

Since the incongruent melting point T_{imp} of $C_{60}\cdot 2B$ is known, along with enthalpy changes for dissolution and melting of the solid phases, the temperature dependence of C_{60} solubility in this solvent can be predicted from its value at a single temperature. Figure 5 shows the phase diagram for the C_{60}/bromobenzene system. The predicted solubility curve (Figure 5b) is adjusted to the experimental solubility[17] of 3.3 mg/mL at 298 K, which represents the solubility of $C_{60}\cdot 2B$, not C_{60}. The portion of the solubility curve above 350 K represents the solubility of pure C_{60}. If extrapolated to 298 K, it represents the hypothetical solubility of pure C_{60} at room temperature, an unachievable state. However, by arguments similar to those presented above, it can be shown that the formation of the solvate lowers the solubility of C_{60} in bromobenzene by a factor of 12.5, compared to hypothetical pristine C_{60} in equilibrium with liquid B at $T = 298$ K. Using a theoretical linear free energy relationship, Smith et al.[18] attempted to correlate the solubility of C_{60} in over 100 organic solvents with properties of the solvent such as molecular volume, polarizability, and

HOMO/LUMO energies, but the agreement between observed and predicted solubilities was poor. In this correlation, it was assumed that the solid in equilibrium with the saturated solution was pure C_{60}. But this reference state is unachievable for C_{60} in bromobenzene and probably in most other organic solvents at room temperature. Recalculating the theoretical linear free energy relationship for C_{60} solubility using the hypothetical solubility of C_{60} at 298 K, as determined in this study for bromobenzene, may lead to a better and more explainable correlation and would elucidate intermolecular solute–solvent interactions in fullerene solutions.

Nagano and Tamura[5] used a simple model to estimate the internal energy of formation of a solvated crystal. On the basis of the X-ray data, this simple model was also used for $C_{60}\cdot 2C_6H_5Br$. We assume that the components in the crystal are kept together by the short-range van der Waals forces and that the energy of formation could be calculated from nearest-neighbor interactions only. In the case of $C_{60}\cdot 2C_6H_5Br$, the bonding scheme leads to the equation

$$\Delta U = 3U(C_{60}-C_{60}) + 2U(C_{60}-B) + 10U(C_{60}-B') \quad (10)$$

where ΔU corresponds to the reaction

$$C_{60}\cdot 2C_6H_5Br(s) = C_{60}(g) + 2C_6H_5Br(g) \quad (11)$$
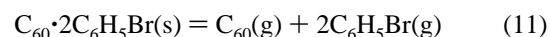
and B and B′ correspond to two orientations of bromobenzene. The $U(C_{60}-C_{60})$ intermolecular bond energy is derived to be 30 kJ/mol from the sublimation enthalpy of C_{60} at 298 K.[19] The value of $U(B-B)$ is 8.8 kJ/mol, estimated from the enthalpy of fusion and enthalpy of evaporation of bromobenzene[20] by assuming that in the solid phase a bromobenzene molecule has 12 nearest neighbors. The Lorenz–Berthold rule was used to estimate roughly the bond energy of intermolecular interaction of C_{60} with bromobenzene. Both contacts were assumed equal: $U(C_{60}-B') = U(C_{60}-B) = \sqrt{(U(C_{60}-C_{60})U(B-B))} = 16.2$ kJ/mol.

From eq 10 ΔU was estimated to be 284 kJ/mol. This quantity can also be calculated based on the experimental value of ΔH for reaction 5, the enthalpy of sublimation of C_{60}, and the enthalpy of evaporation of bromobenzene. In this case, $\Delta U = \Delta H - 3RT = 303$ kJ/mol. Considering that the method used for the estimations of eq 10 is rather crude, the agreement between the two numbers is surprisingly close.

The solvated crystal is kept together by the short-ranged van der Waals interactions of C_{60} with C_{60} and of C_{60} with bromobenzene. The solvate is more stable than typical C_{60} solvates with halogenated alkanes or alkanes, the ΔH_5 per mole of solvent being -21, -3.4, and nearly zero, in units of kJ/mol, for $C_{60}\cdot 2C_6H_5Br$, $C_{60}\cdot 13CCl_4$,[5] and $C60\cdot C_7H_{16}$,[2] respectively. It is interesting to note that according to X-ray data from the present study the rotation of C_{60} in the solvate is hindered at room temperature. Since no orientational phase transition was seen with DSC up to the incongruent melting point of the solvate, it could be stated that the intermolecular interactions that hold this crystal together also prevent rotation over the temperature region where it is stable. In contrast, He et al.[21] concluded from NMR measurements on the C_{60}-solvated crystal with benzene, $C_{60}\cdot 4C_6H_6$, the rotation of the C_{60} is not hindered at room temperature. More experimental work is needed in order to understand the nature of differences between benzene and bromobenzene solvates.

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