



## Enthalpies of dissolution of C<sub>60</sub> and C<sub>70</sub> in *o*-xylene, toluene, and CS<sub>2</sub> at temperatures from 293.15 K to 313.15 K

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Enthalpies of dissolution of C<sub>60</sub> and C<sub>70</sub> in *o*-xylene, toluene, and CS<sub>2</sub> have been measured by a Calvet MS-80 microcalorimeter at temperatures from 293.15 K to 313.15 K. It was observed that the dissolution of C<sub>60</sub> in the three organic solvents in the above range of temperatures was exothermic, while the dissolution of C<sub>70</sub> in the same three solvents was endothermic. The enthalpy of dissolution of C<sub>70</sub> showed a minimum at 308.15 K. The experimental results were discussed. © 1996 Academic Press Limited

### 1. Introduction

Some reports<sup>(1–4)</sup> have appeared in the literature over the past few years on the solubility of C<sub>60</sub> in organic solvents. There is interest in the solubility of C<sub>60</sub> and C<sub>70</sub> because they have a crucial role in the choice of solvents during the process of extraction, isolation, and purification of fullerenes. However, another aspect of data with regard to the dissolution of fullerenes, the enthalpies of dissolution, have not been reported. We consider that the enthalpies of dissolution are of the same importance as solubility because they may have both practical and fundamental interest. Fullerenes are cage-like molecules of carbon and they will probably interact with solvent molecules in ways that provide new information on the mechanisms of (solute + solvent) interactions. A deeper understanding of the interaction of fullerenes with various solvents will allow rational choice of solvents capable of purifying the fullerenes, using cheap and efficient methods.

### 2. Experimental

The purities of C<sub>60</sub> and C<sub>70</sub> were mass fraction 0.99 and > 0.98, respectively, verified by high performance liquid chromatography (h.p.l.c.). Before determining the

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enthalpies of dissolution of  $C_{60}$  and  $C_{70}$  in the solvents, pellets were smashed and powdered. These powders were dried at  $T = 373.15$  K in a vacuum oven for 5 h and preserved in a desiccator.

All solvents were of A.R. grade from the Beijing Chemical Factory, China, and were purified twice through a 1.5 m long rectifying column. The refractive indices of *o*-xylene, toluene, and  $CS_2$  obtained were 1.5049, 1.4968 and 1.6270 at  $T = 293.15$  K respectively and the densities were (0.87516, 0.86247, and 1.2557)  $g \cdot cm^{-3}$  at  $T = 298.15$  K respectively. All the data were in accord with the literature.<sup>(5)</sup>

A Calvet MS-80 microcalorimeter was used for the measurements of the enthalpies of dissolution. The improved reaction cell is shown in figure 1. Volumes of 4  $cm^3$  of solvent were placed in both the reaction cell and the control cell. A quantity of  $C_{60}$  or  $C_{70}$  was added to the glass cup in the reaction cell; nothing was added to the glass cup in the control cell. Dissolution was started by completely turning the microcalorimetric body down and up five times or more until the machine came to thermal equilibrium. Each experiment was repeated at least twice.

The solubility of  $C_{60}$  and  $C_{70}$  in organic solvents was rather low.<sup>(1-4)</sup> In this experiment, only (1.5 to 8.5) mg of sample of  $C_{60}$  or  $C_{70}$  was dissolved in 4  $cm^3$  of solvents, and the process of dissolution sometimes lasted longer than 3 h. Therefore, to ensure the complete dissolution of  $C_{60}$  or  $C_{70}$  in the solvents, the solution was checked very carefully after every experiment in order to ensure that no solid remained.

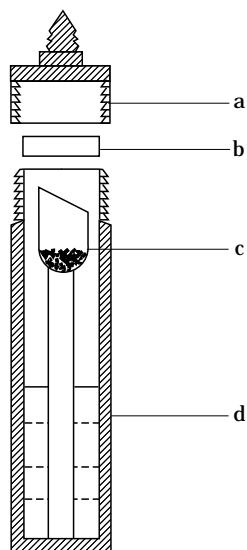


FIGURE 1. A sketch of the improved reaction cell: (a) stainless lid; (b) Teflon seal; (c) small glass cup (0.5  $cm^3$ ); (d) stainless reaction cell (12  $cm^3$ ).

### 3. Results

The measured enthalpies of dissolution for C<sub>60</sub> and C<sub>70</sub> in *o*-xylene, toluene, and CS<sub>2</sub> are listed in tables 1 and 2 respectively. From the temperatures 293.15 K to 313.15 K, the dissolution of C<sub>60</sub> in *o*-xylene, toluene, and CS<sub>2</sub> is exothermic, characterized by the negative value of  $\Delta_{sol}H$ . In contrast, the dissolution of C<sub>70</sub> in the same three solvents is endothermic, characterized by a positive value of  $\Delta_{sol}H$ . From the tables, the heat effect measured ( $\Delta_{sol}H$ ) is quite small (only about 0.001 J to 0.06 J) when a small sample of C<sub>60</sub> or C<sub>70</sub> was dissolved in 4 cm<sup>3</sup> of the solvent.

TABLE 1. The enthalpies of dissolution of C<sub>60</sub> in *o*-xylene, toluene and CS<sub>2</sub> at temperatures from 293.15 K to 313.15 K, where  $W$  is the mass of C<sub>60</sub>,  $m$  is the molality of C<sub>60</sub> solutions,  $\Delta_{sol}H$  is the enthalpy of dissolution of mass  $W$  of C<sub>60</sub> in 4 cm<sup>3</sup> of solvents,  $\Delta_{sol}H_m$  is the molar enthalpy of dissolution of C<sub>60</sub> in the solvents, and  $\overline{\Delta_{sol}H_m}$  is the average molar enthalpy of dissolution of C<sub>60</sub> in the solvents over two measurements

$T$ K	$W$ g	$m$ mol·kg <sup>-1</sup>	$\Delta_{sol}H$ J	$\Delta_{sol}H_m$ kJ·mol <sup>-1</sup>	$\overline{\Delta_{sol}H_m}$ kJ·mol <sup>-1</sup>
solvent: <i>o</i> -xylene					
293.15	0.00390	0.001550	-0.0593	-11.0	
	0.00417	0.001650	-0.0650	-11.2	-11.1 ± 0.1
298.15	0.00340	0.001339	-0.0505	-10.7	
	0.00364	0.001438	-0.0546	-10.8	-10.8 ± 0.1
303.15	0.00398	0.001566	-0.0587	-10.6	
	0.00402	0.001577	-0.0595	-10.7	-10.7 ± 0.1
308.15	0.00400	0.001573	-0.0578	-10.4	
	0.00406	0.001593	-0.0584	-10.4	-10.4 ± 0.0
313.15	0.00397	0.001573	-0.0554	-10.1	
	0.00394	0.001558	-0.0556	-10.2	-10.2 ± 0.1
solvent: toluene					
293.15	0.00229	0.000932	-0.0242	-7.62	
	0.00232	0.000941	-0.0245	-7.61	-7.62 ± 0.01
298.15	0.00234	0.000931	-0.0245	-7.55	
	0.00232	0.000926	-0.0242	-7.52	-7.54 ± 0.02
303.15	0.00227	0.000923	-0.0235	-7.46	
	0.00227	0.000902	-0.0234	-7.43	-7.45 ± 0.02
308.15	0.00224	0.000890	-0.0228	-7.34	
	0.00230	0.000916	-0.0235	-7.36	-7.35 ± 0.01
313.15	0.00231	0.000918	-0.0233	-7.27	
	0.00231	0.000919	-0.0234	-7.30	-7.29 ± 0.02
solvent: CS <sub>2</sub>					
293.15	0.00425	0.001178	-0.0446	-7.56	
	0.00470	0.001301	-0.0489	-7.51	-7.53 ± 0.03
298.15	0.00467	0.001290	-0.0092	-1.42	
	0.00464	0.001282	-0.0095	-1.48	-1.45 ± 0.03
303.15	0.00460	0.001334	-0.0056	-0.88	
	0.00458	0.001264	-0.0059	-0.93	-0.91 ± 0.03
308.15	0.00465	0.001278	-0.0055	-0.85	
	0.00475	0.001309	-0.0056	-0.85	-0.85 ± 0.00
313.15	0.00464	0.001276	-0.0053	-0.82	
	0.00463	0.001263	-0.0054	-0.84	-0.83 ± 0.01

TABLE 2. The enthalpies of dissolution of  $C_{70}$  in *o*-xylene, toluene, and  $CS_2$  at temperatures from 293.15 K to 313.15 K, where  $W$  is the mass of  $C_{70}$ ,  $m$  is the molality of  $C_{70}$  solutions,  $\Delta_{sol}H$  is the enthalpy of dissolution of mass  $W$  of  $C_{70}$  in 4 cm<sup>3</sup> of solvent,  $\Delta_{sol}H_m$  is the molar enthalpy of dissolution of  $C_{70}$  in the solvents, and  $\overline{\Delta_{sol}H_m}$  is the average molar enthalpy of dissolution of  $C_{70}$  in the solvents over two measurements

$T$ K	$W$ g	$m$ mol·kg <sup>-1</sup>	$\Delta_{sol}H$ J	$\Delta_{sol}H_m$ kJ·mol <sup>-1</sup>	$\overline{\Delta_{sol}H_m}$ kJ·mol <sup>-1</sup>
solvent: <i>o</i> -xylene					
293.15	0.00699	0.002352	0.0270	3.25	
	0.00700	0.002355	0.0272	3.27	3.26 ± 0.01
298.15	0.00683	0.002369	0.0154	1.90	
	0.00675	0.002345	0.0157	1.96	1.93 ± 0.03
303.15	0.00698	0.002355	0.0127	1.53	
	0.00725	0.002440	0.0128	1.48	1.51 ± 0.03
308.15	0.00703	0.002366	0.0112	1.34	
	0.00695	0.002339	0.0107	1.29	1.32 ± 0.03
313.15	0.00699	0.002352	0.0132	1.59	
	0.00701	0.002358	0.0125	1.50	1.55 ± 0.05
solvent: toluene					
293.15	0.00161	0.000547	0.0055	2.87	
	0.00154	0.000528	0.0051	2.78	2.83 ± 0.05
298.15	0.00163	0.000558	0.0026	1.34	
	0.00160	0.000546	0.0027	1.42	1.38 ± 0.04
303.15	0.00152	0.000517	0.0012	0.66	
	0.00157	0.000537	0.0013	0.70	0.68 ± 0.02
308.15	0.00151	0.000516	0.0008	0.45	
	0.00152	0.000518	0.0009	0.50	0.48 ± 0.03
313.15	0.00161	0.000550	0.0013	0.68	
	0.00358	0.001221	0.0026	0.61	0.65 ± 0.04
solvent: $CS_2$					
293.15	0.00842	0.001991	0.0338	3.38	
	0.00847	0.002012	0.0345	3.42	3.40 ± 0.02
298.15	0.00813	0.001929	0.0209	2.16	
	0.00798	0.001893	0.0200	2.11	2.14 ± 0.03
303.15	0.00828	0.001935	0.0159	1.61	
	0.00801	0.001882	0.0161	1.69	1.65 ± 0.04
308.15	0.00805	0.001907	0.0110	1.15	
	0.00905	0.002159	0.0126	1.17	1.16 ± 0.01
313.15	0.00798	0.001892	0.0185	1.95	
	0.00797	0.001892	0.0177	1.87	1.91 ± 0.04

The temperature dependence of the enthalpies of dissolution of  $C_{60}$  and  $C_{70}$  are shown in figures 2 and 3 respectively. The sequence of  $\Delta_{sol}H$  of  $C_{60}$  in the three solvents at all five temperatures is:  $CS_2 >$  toluene  $>$  *o*-xylene; while the sequence of  $C_{70}$  at all the temperatures except 308.15 K is:  $CS_2 >$  *o*-xylene  $>$  toluene and at 308.15 K is: *o*-xylene  $>$   $CS_2 >$  toluene. As the temperature rises,  $\Delta_{sol}H$  of  $C_{60}$  in *o*-xylene and toluene increases slightly, while in  $CS_2$ , the  $\Delta_{sol}H$  of  $C_{60}$  rises markedly and then levels off. The  $\Delta_{sol}H$  of  $C_{70}$  in all three solvents decreases with the increase of temperature from 293.15 K to 308.15 K,  $\Delta_{sol}H$  then rises to a minimum at  $T = 308.15$  K.

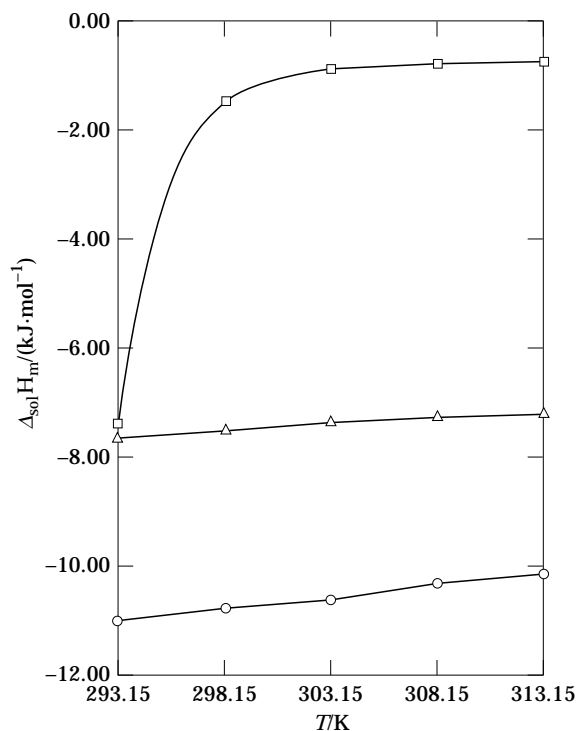


FIGURE 2. The temperature dependence of the molar enthalpies of dissolution  $\Delta_{\text{sol}}H_m$  of C<sub>60</sub>: ○, *o*-xylene; △, toluene; □, carbon disulfide.

#### 4. Discussion

The dissolution of C<sub>60</sub> and C<sub>70</sub> in organic solvents involves two kinds of energy effect: one is the crystal dissociation energy caused by the solvent molecules acting on the molecules of C<sub>60</sub> or C<sub>70</sub> at the crystal lattice points; another is the solvation energy released when certain kinds of interaction between fullerene and solvent molecules occurred. The enthalpy of dissolution is the difference between these two kinds of energy. Solid C<sub>60</sub> and C<sub>70</sub> exhibit opposing heat effects during their dissolution: C<sub>60</sub> is exothermic while C<sub>70</sub> is endothermic. This indicates that during the dissolution of C<sub>60</sub> the solvation energy released exceeds the crystal dissociation energy absorbed, in contrast to the dissolution of C<sub>70</sub>, where the solvation energy released is less than the crystal dissociation energy absorbed.

Pan *et al.*<sup>(6)</sup> measured the enthalpies of sublimation of C<sub>60</sub> and C<sub>70</sub> as  $(167.8 \pm 5.4)$  kJ·mol<sup>-1</sup> and  $(179.9 \pm 9.2)$  kJ·mol<sup>-1</sup>, respectively, at average temperatures of 707 K and 739 K. Guo *et al.*<sup>(7)</sup> also gave similar results through theoretical calculation. These results suggest that the crystal dissociation energy in a solution of C<sub>70</sub> is a little larger than that of C<sub>60</sub>.

Molecules of C<sub>60</sub> and C<sub>70</sub> have closed hollow carbon cage structures with symmetries of *I<sub>h</sub>* and *D<sub>5h</sub>* respectively. The inner and outer surfaces are covered with

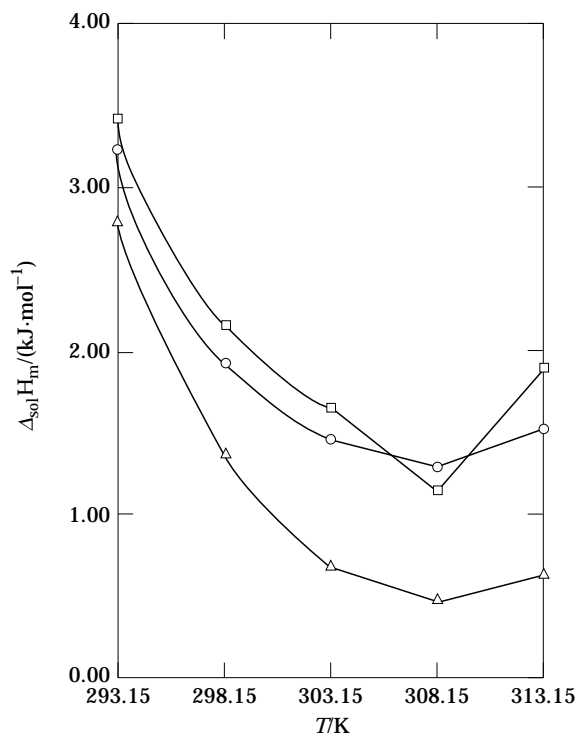


FIGURE 3. The temperature dependence of the molar enthalpies of dissolution  $\Delta_{\text{sol}}H_m$  of  $C_{70}$ :  $\circ$ , o-xylene;  $\triangle$ , toluene;  $\square$ , carbon disulfide.

a sea of  $\pi$  electrons. There are two types of C–C bond lengths in a  $C_{60}$  molecule (hexagon–hexagon fusions: 0.140 nm; hexagon–pentagon fusions: 0.145 nm). A  $C_{60}$  molecule has more resonance structures than  $C_{70}$  because of its higher symmetry.<sup>(8)</sup> This suggests that the  $\pi$  electrons are easier to delocalize in a  $C_{60}$  molecule than in a  $C_{70}$  molecule. However, in a  $C_{70}$  molecule, there are eight symmetry-inequivalent C–C bond lengths ranging between 0.138 nm and 0.148 nm. So many inequivalent C–C bond lengths are unfavourable for resonance. Nikolaev *et al.*<sup>(9)</sup> accurately determined the structure of the  $C_{70}$  molecule and pointed out that the equatorial region of a  $C_{70}$  molecule should be chemically inert because of the existence of the longest C–C bonds of the molecule. On the other hand, the polar regions exhibit bond patterns reminiscent of  $C_{60}$  and mimic its chemical behaviour. Thus the  $C_{60}$  molecules are more polarizable than  $C_{70}$ , and  $C_{60}$  will release a larger solvation energy than  $C_{70}$  in the same solvent.

Since the change in temperature is relatively small in this experiment, the lattice structure of crystal  $C_{60}$  is unlikely to show any transformation from  $T = 293.15$  K to  $T = 313.15$  K. There will, therefore, be little change in crystal dissociation energy while temperature rises. Warming increases the speed of the thermal motion of the solute and solvent molecules in solution, thus the solvation energy will decrease

when the temperature increases. When the temperature rises to near the boiling temperature of CS<sub>2</sub>, the solvation energy of C<sub>60</sub> in CS<sub>2</sub> reduces rapidly. This is why the enthalpies of dissolution of C<sub>60</sub> in three solvents all increase with the rise in temperature and, in CS<sub>2</sub>, it showed a marked lift.

The temperature dependence of the enthalpies of dissolution of C<sub>70</sub> is more complex. The dissolution of C<sub>70</sub> is endothermic and we should expect the  $\Delta_{sol}H$  of C<sub>70</sub> to increase with the rise of temperature because of the reduction in solvation energy. Our results show that  $\Delta_{sol}H$  becomes smaller on warming. We suspect such a decrease of  $\Delta_{sol}H$  to be related to the phase transition of C<sub>70</sub> at  $T = 307$  K.<sup>(10)</sup>

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