



Enthalpies of dissolution of C₆₀ and C₇₀ in *o*-xylene, toluene, and CS₂ at temperatures from 293.15 K to 313.15 K

Jun Yin,^a Bao-Huai Wang,^b Zhi-Fen Li, and You-Min Zhang

Institute of Physical Chemistry, Peking University, Beijing 100871, P.R. China

Xi-Huang Zhou and Zhen-Nan Gu

Department of Chemistry, Peking University, Beijing 100871, P.R. China

Enthalpies of dissolution of C₆₀ and C₇₀ in *o*-xylene, toluene, and CS₂ 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 C₆₀ in the three organic solvents in the above range of temperatures was exothermic, while the dissolution of C₇₀ in the same three solvents was endothermic. The enthalpy of dissolution of C₇₀ showed a minimum at 308.15 K. The experimental results were discussed. © 1996 Academic Press Limited

1. Introduction

Some reports^(1–4) have appeared in the literature over the past few years on the solubility of C₆₀ in organic solvents. There is interest in the solubility of C₆₀ and C₇₀ 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 C₆₀ and C₇₀ were mass fraction 0.99 and > 0.98, respectively, verified by high performance liquid chromatography (h.p.l.c.). Before determining the

^a Present address: Department of Chemistry, Rutgers — The State University of New Jersey, Piscataway, NJ 08855-0939, U.S.A.

^b To whom correspondence should be addressed.

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.⁽⁵⁾

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.⁽¹⁻⁴⁾ 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.

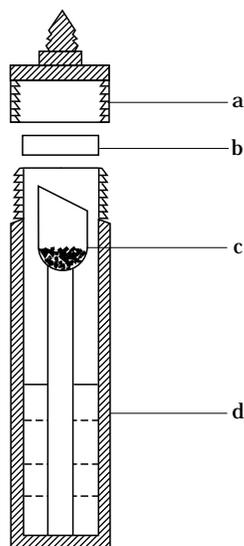


FIGURE 1. A sketch of the improved reaction cell: (a) stainless lid; (b) Teflon seal; (c) small glass cup (0.5 cm^3); (d) stainless reaction cell (12 cm^3).

3. Results

The measured enthalpies of dissolution for C₆₀ and C₇₀ in *o*-xylene, toluene, and CS₂ are listed in tables 1 and 2 respectively. From the temperatures 293.15 K to 313.15 K, the dissolution of C₆₀ in *o*-xylene, toluene, and CS₂ is exothermic, characterized by the negative value of $\Delta_{sol}H$. In contrast, the dissolution of C₇₀ 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 C₆₀ or C₇₀ was dissolved in 4 cm³ of the solvent.

TABLE 1. The enthalpies of dissolution of C₆₀ in *o*-xylene, toluene and CS₂ at temperatures from 293.15 K to 313.15 K, where W is the mass of C₆₀, m is the molality of C₆₀ solutions, $\Delta_{sol}H$ is the enthalpy of dissolution of mass W of C₆₀ in 4 cm³ of solvents, $\Delta_{sol}H_m$ is the molar enthalpy of dissolution of C₆₀ in the solvents, and $\overline{\Delta_{sol}H_m}$ is the average molar enthalpy of dissolution of C₆₀ in the solvents over two measurements

T K	W g	m mol·kg ⁻¹	$\Delta_{sol}H$ J	$\Delta_{sol}H_m$ kJ·mol ⁻¹	$\overline{\Delta_{sol}H_m}$ kJ·mol ⁻¹
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 ₂					
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 cm³ 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 ⁻¹	$\Delta_{sol}H$ J	$\Delta_{sol}H_m$ kJ·mol ⁻¹	$\overline{\Delta_{sol}H_m}$ kJ·mol ⁻¹
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.

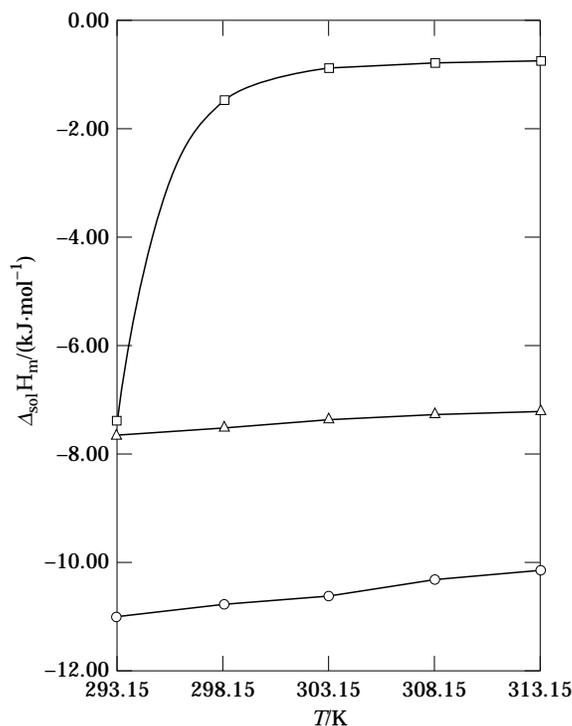


FIGURE 2. The temperature dependence of the molar enthalpies of dissolution $\Delta_{\text{sol}}H_m$ of C₆₀: ○, *o*-xylene; △, toluene; □, carbon disulfide.

4. Discussion

The dissolution of C₆₀ and C₇₀ 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 C₆₀ or C₇₀ 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 C₆₀ and C₇₀ exhibit opposing heat effects during their dissolution: C₆₀ is exothermic while C₇₀ is endothermic. This indicates that during the dissolution of C₆₀ the solvation energy released exceeds the crystal dissociation energy absorbed, in contrast to the dissolution of C₇₀, where the solvation energy released is less than the crystal dissociation energy absorbed.

Pan *et al.*⁽⁶⁾ measured the enthalpies of sublimation of C₆₀ and C₇₀ as (167.8 ± 5.4) kJ·mol⁻¹ and (179.9 ± 9.2) kJ·mol⁻¹, respectively, at average temperatures of 707 K and 739 K. Guo *et al.*⁽⁷⁾ also gave similar results through theoretical calculation. These results suggest that the crystal dissociation energy in a solution of C₇₀ is a little larger than that of C₆₀.

Molecules of C₆₀ and C₇₀ have closed hollow carbon cage structures with symmetries of *I_h* and *D_{5h}* respectively. The inner and outer surfaces are covered with

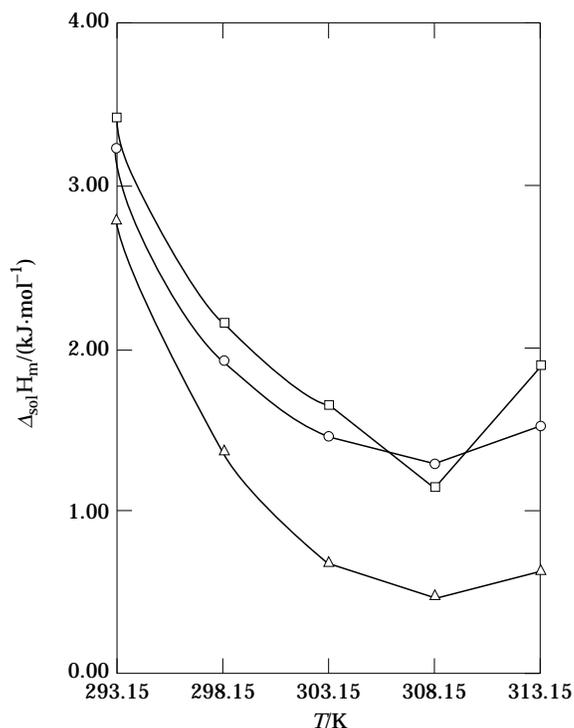


FIGURE 3. The temperature dependence of the molar enthalpies of dissolution $\Delta_{\text{sol}}H_m$ of C_{70} : \circ , o-xylene; \triangle , toluene; \square , carbon disulfide.

a sea of π 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.⁽⁸⁾ This suggests that the π 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.*⁽⁹⁾ 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 CS₂, the solvation energy of C₆₀ in CS₂ reduces rapidly. This is why the enthalpies of dissolution of C₆₀ in three solvents all increase with the rise in temperature and, in CS₂, it showed a marked lift.

The temperature dependence of the enthalpies of dissolution of C₇₀ is more complex. The dissolution of C₇₀ is endothermic and we should expect the $\Delta_{sol}H$ of C₇₀ 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 C₇₀ at $T = 307\text{ K}$.⁽¹⁰⁾

REFERENCES

1. Sivaraman, N.; Dhamodaran, R.; Kaliappan, I. *J. Org. Chem.* **1992**, *57*, 6077.
2. Ruoff, R. S.; Tse, D. S.; Malhotra, R. *J. Phys. Chem.* **1993**, *97*, 3379.
3. Ruoff, R. S.; Malhotra, R.; Huestis, D. L. *Nature* **1993**, *362*, 140.
4. Zhou, X.; Gu, Z.; Wu, Y. *Carbon* **1994**, *32*, 935.
5. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Vol. 2: Organic Solvents*, 4th edition. Wiley: New York, **1986**.
6. Pan, C.; Sampson, M. P.; Chai, Y. *J. Phys. Chem.* **1991**, *95*, 2944.
7. Guo, Y.; Karasawa, N.; Goddard, W. A. *Nature* **1991**, *351*, 464.
8. Kroto, H. W. *Nature* **1987**, *329*, 529.
9. Nikolaev, A. V.; John, T.; Prassides, K. *Chem. Phys. L.* **1994**, *7*, 17.
10. Sworakowski, J.; Palewska, K.; Bertault, M. *Chem. Phys. L.* **1994**, *4*, 1.

(Received 4 December 1995; in final form 16 April 1996)

WA-089