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Polythermal study of C_{60} solubility in tetralin

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The polythermal analysis of C_{60} fullerene in tetralin has been carried out by means of solubility and differential scanning calorimetry methods in a wide temperature range.

Fullerenes are the only carbon species soluble in organic solvents.[1] Studies of fullerene solubility in various solvents were mainly performed at 298.15 K.[2–8] In this context, the polythermal studies of C_{60} solutions are very important for calculating the thermodynamic parameters of dissolution and better understanding the interactions in fullerenes solutions. We accurately measured the solubility of C_{60} in pure tetralin (1,2,3,4-tetrahydronaphthalene) in a wide temperature range and calculated the thermodynamic parameters of C_{60} solutions from the solubility data. The formation of a solid solvate of C_{60} fullerene with tetralin is also an important finding.

The samples of C_{60} fullerene (99.9% purity) were collected from Fullerenes Technologies Ltd. (St. Petersburg, Russia). Tetralin (99% purity) was obtained from Sigma-Aldrich and used without further purification.

The saturation was carried out using 1 ml glass ampoules fixed in a thermostat at an angle of 45° and rotated at 10 rpm. The temperature was kept to within ±0.05 K. According to our preliminary experiments, the saturation requires about 48 h to complete. After mixing, the ampoules were kept at the experiment temperature for 15 h. The fullerene concentrations were measured to within 5% by liquid chromatography using the Multichrom 1.5 program package.

The thermoanalysis of C_{60}–tetralin samples was performed using a DCS 204 F1 Phoenix differential scanning calorimeter (Netzsch). Each sample was scanned several times within the temperature range 188–373 K. The scanning rate was 10 K min^{-1}. Before DSC measurements, one set of samples was kept at 260±2 K during a period of several days to a month. The other set of samples was stored at 293 K. The detailed technique of crystallosolvate detection was described elsewhere.[9–11]

The measured solubilities of C_{60} in tetralin are collected in Table 1. The solubility of C_{60} increases monotonously at 298–338 K, reaching a maximum solubility at 341 K. The solubility data for temperatures up to 328 K are in good agreement with results obtained previously[12] (a maximum solubility of C_{60} in tetralin at 329 K, which is 12 K lower than our value). According to published data,[2,11,13–15] the anomalous behaviour of saturated fullerene solutions is due to the formation and decomposition of solid solvates (crystallosolvates) of fullerenes with solvent molecules. After crystallosolvate decomposes, the properties of the saturated solution change dramatically because of a change in bottom phase composition, which is in equilibrium with the saturated solution. The change of the heat of solution from endothermic to exothermic will result in the appearance of a maximum in the temperature dependence of solubility.

Table 1 Solubility of C_{60} fullerene in tetralin at different temperatures.

T/K	Solubility/mg cm^{-3}	T/K	Solubility/mg cm^{-3}
298	12.23	343	39.47
308	15.19	345	31.35
318	17.06	348	29.12
328	22.61	353	27.62
338	25.52	358	24.68
340	30.19	363	19.75
341	40.37	368	17.52

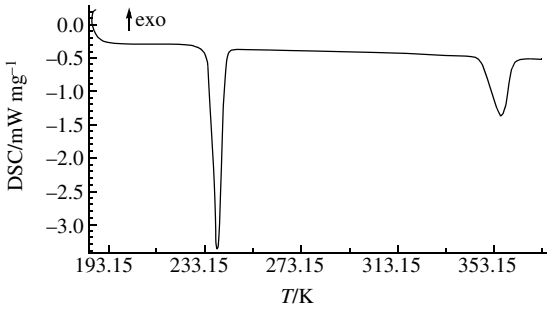

Figure 1 DSC curve of the C_{60}–tetralin system.

The enthalpy of fullerene solution can be calculated using the temperature dependence of solubility and the equation

$$\frac{\mathrm{d}\ln X}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sol}}H^0}{RT^2}. \quad (1)$$

The thermodynamic functions of fullerene sublimation and those obtained from equation (1) allowed us to calculate the thermodynamic characteristics of fullerene solvation.

Let us discuss the DSC investigation of the C_{60}–tetralin system. The DSC curves allowed us to determine the temperature, enthalpy and entropy of incongruent melting and the composition of solid solvates.[16] A typical DSC curve for the test system is shown in Figure 1. The first peak in the curve corresponds to excess solvent melting, whereas the second endothermic peak corresponds to the decomposition of fullerene crystallosolvate. The temperature when the crystallosolvate starts to decompose (348 K) corresponds to a maximum in the C_{60} solubility. To verify this we scanned all of the samples and obtained nearly the same results. Therefore, we suppose that the crystallosolvate in the C_{60}–tetralin system is stable, and it has a short formation time (~1 h). The stoichiometric ratio

Table 2 Thermodynamic characteristics of the C_{60} crystallosolvate observed in tetralin.

T_{imp}/K	$\Delta_{\mathrm{r}}H$/kJ mol^{-1}	$\Delta_{\mathrm{r}}S$/J mol^{-1} s^{-1}	Composition, N_f:N_{trl}
347.7±0.3	29±1 (30)[a]	84±3 (86)	1:(2.0±0.1)

[a]The values estimated from solubility data are given in parentheses.

fullerene:solvent in the crystallosolvate was found using the equation[16]

$$n = \left(\frac{m(\mathrm{S})}{M(\mathrm{S})} - \frac{\Delta H_{\mathrm{exc}}}{\Delta_{\mathrm{fus}} H} \right) \Big/ \frac{m(\mathrm{C_{60}})}{M(\mathrm{C_{60}})}. \quad (2)$$

Here, $m(C_{60})$ and $m(S)$ are the fullerene and solvent masses (mg) in the sample, respectively; $M(C_{60})$ and $M(S)$ are the fullerene and solvent molecular weights (g mol^{-1}), respectively; ΔH_{exc} is the heat of excess solvent melting (J); $\Delta_{fus}H$ is the melting enthalpy (J mol^{-1}) of pure solvent. The thermodynamic parameters (temperature T_{imp}, enthalpy $\Delta_r H$ and entropy $\Delta_r S$) of incongruent melting and the composition of the crystallosolvate are summarised in Table 2.

According to DSC data, a crystallosolvate, which has an incongruent melting temperature of about 348 K, occurs in the test system. Crystallosolvate melting produces pure fullerene and the solvent:

$$C_{60}\cdot 2C_{10}H_{12} \rightarrow C_{60} + 2C_{10}H_{12},\ \Delta_r H = 29\pm1 \text{ kJ mol}^{-1}. \quad (3)$$

The thermodynamic parameters of C_{60} solution and solvation in tetralin can be derived from the temperature dependence of solubility. Since there is a crystallosolvate in the C_{60}–tetralin system, the standard thermodynamic functions were calculated using the solubility values x^{hyp}, which represent the hypothetic solubility of C_{60}, *i.e.*, considering the fact that solid phase is composed of pure C_{60} rather than the C_{60} crystallosolvate.[11,17–19] Note that $x^{hyp} = x^{exp}$ after a maximum. The thermodynamic functions were calculated using the following equations:[11]

$$\Delta_{sol}G^0 = -RT\ln x + \Delta_r G^0 = -RT\ln x^{hyp}, \quad (4)$$

$$\Delta_{sol}H^0 = RT^2 \frac{\partial \ln x}{\partial T} + \Delta_r H^0, \quad (5)$$

$$\Delta_{sol}S^0 = \frac{\Delta_{sol}H^0}{T} + R\ln x^{hyp}, \quad (6)$$

$$x^{hyp} = -\frac{\Delta_r G^0}{RT} x^{exp}, \quad (7)$$

where $\Delta_r G^0 = \Delta_r H^0(1 - T/T_{imp})$ is the Gibbs free energy of the crystallosolvate formation reaction ($C_{60(s)} + 2C_{10}H_{12(liq)} \rightarrow C_{60}\cdot 2C_{10}H_{12}$), $\Delta_r H^0$ and T_{imp} are the enthalpy and temperature of incongruent melting of the crystallosolvate, respectively.

The entropy of incongruent melting can be calculated considering this process as a phase transition $\Delta_r S = \Delta_r H/T_{imp}$ and that the $\Delta_r H$ and $\Delta_r S$ are temperature independent. The thermodynamic parameters of C_{60} in the form of an ideal gas[20] were used in the calculations of C_{60} solvation parameters (Table 3). The enthalpy of C_{60} solution in tetralin was estimated according to equation (1) using hypothetical (x^{hyp}) and experimental (x^{exp}) solubility values in the whole temperature range.

Table 3 Thermodynamic functions (ΔH^0, ΔG^0 in kJ mol^{-1}, ΔS^0 in J mol^{-1} K^{-1}) of solution and solvation of C_{60} in tetralin.[a]

T/K	$-\ln x$	$-\Delta_{sol}H^0$	$\Delta_{sol}G^0$	$-\Delta_{sol}S^0$	$-\Delta_{solv}H^0$	$\Delta_{solv}G^0$	$-\Delta_{solv}S^0$
298.15	**4.4**	13	**11**	**81**	197	**135**	**208**
308.15	**4.5**	13	**12**	**81**	197	**133**	**207**
318.15	**4.8**	13	**13**	**81**	197	**131**	**207**
328.15	**4.8**	13	**13**	**80**	197	**130**	**205**
338.15	**5.0**	13	**14**	**81**	197	**128**	**204**
340.15	**4.9**	13	**14**	**80**	197	**128**	**203**
341.15	**4.6**	13	**13**	**77**	197	**129**	**201**
343.15	4.8	13	14	79	197	128	202
345.15	5.1	13	15	81	197	126	204
348.15	5.1	13	15	81	197	126	204
353.15	5.2	13	15	81	197	125	203
358.15	5.3	13	16	81	197	124	203
363.15	5.5	13	17	83	197	123	204
368.15	5.6	13	17	83	197	122	204

[a]Thermodynamic characteristics calculated from hypothetical solubility values are marked in bold.

The results of our calculations indicate that the positive Gibbs free energy of C_{60} solution $\Delta_{sol}G^0$ is due to the significant contribution of the entropy term. The enthalpy of C_{60} sublimation is temperature independent within the test temperature range; therefore, the enthalpy of C_{60} solvation $\Delta_{solv}H^0$ is constant. $\Delta_{solv}H^0$ gives the major contribution into the Gibbs free energy of C_{60} solvation $\Delta_{solv}G^0$, which is negative. On the other hand, the temperature dependence of $\Delta_{solv}G^0$ is controlled by the entropy term, and its contribution increases with temperature. As a result, the C_{60} solvation is more favourable at low temperatures.

The values of $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ for solubility data, where C_{60} solubility increases with temperature, may be obtained from equation (1). Then, thermodynamic functions of crystallosolvate decomposition ($\Delta_r H$ and $\Delta_r S$) may be estimated (these parameters normally can be obtained using DSC). The values of $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ correspond to the crystallosolvate and the difference between them and those values for pure fullerene represents the enthalpy and entropy of incongruent melting of crystallosolvate. The calculated $\Delta_r H$ and $\Delta_r S$ (shown in Table 2 in parentheses) are in good agreement with the experimental values.

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References

1 V. N. Bezmelnitsyn, A. V. Eletskii and M. V. Okun, *Usp. Fiz. Nauk*, 1998, **168**, 1195 (*Phys. Usp*., 1998, **41**, 1091).
2 Y. Marcus, A. Smith, M. V. Korobov, A. L. Mirakyan, N. V. Avramenko and E. B. Stukalin, *J. Phys. Chem. B*, 2001, **105**, 2499.
3 D. V. Konarev and R. N. Lyubovskaya, *Usp. Khim*., 1999, **68**, 23 (*Russ. Chem. Rev.*, 1999, **68**, 19).
4 S. M. Danauskas and P. C. Jurs, *J. Chem. Inf. Comput. Sci*., 2001, **41**, 419.
5 E. N. Karaulova and E. I. Bagrii, *Usp. Khim*., 1999, **68**, 979 (*Russ. Chem. Rev.*, 1999, **68**, 889).
6 D. V. Konarev, V. N. Semkin, A. Graja and R. N. Lyubovskaya, *J. Mol. Struct.*, 1998, **450**, 11.
7 I. S. Neretin and Yu. L. Slovokhotov, *Usp. Khim*., 2004, **73**, 492 (*Russ. Chem. Rev.*, 2004, **73**, 455).
8 L. N. Sidorov, M. A. Yurovskaya, A. Ya. Borshchevskii, I. V. Trushkov and I. N. Ioffe, *Fullereny* (*Fullerenes*), Ekzamen, Moscow, 2005 (in Russian).
9 N. V. Avramenko, E. B. Stukalin, M. V. Korobov, I. S. Neretin and Yu. V. Slovokhotov, *Thermochim. Acta*, 2001, **370**, 21.
10 A. L. Smith, E. Walter, M. V. Korobov and O. L. Gurvich, *J. Phys. Chem.*, 1996, **100**, 6775.
11 M. V. Korobov, A. L. Mirakyan, N. V. Avramenko, G. Oloffsson, A. L. Smith and R. S. Ruoff, *J. Phys. Chem. B*, 1999, **103**, 1339.
12 R. J. Doome, A. Fonseca, H. Richter, J. B. Nagy, P. A. Thiry and A. A. Lucas, *J. Phys. Chem. Solids*, 1997, **58**, 1839.
13 M. V. Korobov, A. L. Mirakyan, N. V. Avramenko and R. Ruoff, *Dokl. Akad. Nauk*, 1996, **349**, 346 (in Russian).
14 N. V. Avramenko, A. L. Mirakyan and M. V. Korobov, *Thermochim. Acta*, 1997, **299**, 141.
15 M. T. Beck, *Pure Appl. Chem*., 1998, **70**, 1881.
16 G. Olofsson, I. Wadso and R. S. Ruoff, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, eds. K. M. Kadish and R. S. Ruoff, Electrochem. Soc. Proceedings Series, Pennington, NJ, 1996, vol. PV 96-10, p. 18.
17 A. M. Kolker, N. I. Islamova, N. V. Avramenko and A. V. Kozlov, *Zh. Fiz. Khim.*, 2006, **80**, 1825 (*Russ. J. Phys. Chem*., 2006, **80**, 1622).
18 N. V. Avramenko, M. V. Korobov, A. M. Parfenova, P. A. Dorozhko, N. A. Kiseleva and P. V. Dolgov, *J. Therm. Anal. Calorim.*, 2006, **84**, 259.
19 A. M. Kolker, N. I. Islamova, N. V. Avramenko and A. V. Kozlov, *J. Mol. Liq.*, 2007, **131**, 95.
20 V. V. Dikii and G. Ya. Kabo, *Usp. Khim*., 2000, **69**, 107 (*Russ. Chem. Rev.*, 2000, **69**, 95).

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