Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2005, 15(2), 86–87
Mendeleev Communications

Solubility of C_{60} fullerene in *o*-dichlorobenzene–tetrachloromethane mixtures

Nadezhda I. Islamova,* Andrey N. Kinchin,† Aleksey V. Kozlov and Arkadii M. Kolker

Institute of Solution Chemistry, Russian Academy of Sciences, 153045 Ivanovo, Russian Federation. E-mail: nii@isc-ras.ru

DOI: 10.1070/MC2005v015n02ABEH002007

The solubility of C_{60} fullerene in *o*-dichlorobenzene–tetrachloromethane mixtures has been studied in a wide temperature range, and the thermodynamic functions of C_{60} solution have been calculated.

Fullerene solutions in organic solvents play a key role in the extraction and chromatographic separation of C_{60}, C_{70} and higher fullerenes. The effective separation of fullerenes from the fullerene-containing soot obtained by the high-temperature evaporation of graphite in a helium atmosphere is based on the different solubility of these fullerenes in the organic solvents.

There are experimental data on fullerene solubility in pure solvents[1–11] and only a few studies have been performed to obtain their solubility in binary mixtures of organic solvents.[1,5] The temperature dependence of solubility has been investigated.[2,6–10] In most cases, the maximum on the C_{60} solubility–temperature dependence was observed. This fact may be attributed to the change of the composition of the bottom phase. Information on fullerene solvation mechanisms will allow us to develop selective physico-chemical processes involving fullerenes and to select solvent compositions for the separation of C_{60}/C_{70} mixtures.

Fullerene molecules can form a homogeneous surface structure, which, unlike to the structure formed by planar or elongated molecules, interacts with its surrounding almost independently of their orientation.[12] This unique molecular structure is believed to be the major reason for the unusual behaviour of fullerenes in solutions.

The commercial C_{60} fullerene (99.9% purity) from 'Fullerene Technologies' (St.-Petersburg) was used. Tetrachloromethane (c.p. grade) was purified according to a published procedure.[13] *o*-Dichlorobenzene (99% purity) from Merck was used without additional purification.

The saturation was performed in special 1 ml glass ampoules fixed in a thermostat at an angle of 45°. The ampoules were rotated at a rate of 10 rpm. The temperature was kept to within ±0.05 K using a high-precision temperature regulator. According to our preliminary experiments, the saturation requires ~48 h. After mixing, the ampoules were stored at the temperature of the experiment for 15 h. The fullerene concentration was measured with a Liquochrom Model 2010 chromatograph equipped with a Beckman Model 110A pump, a UV detector (330 nm) and a Separon SGX C18 column (4×250 mm). The column temperature was 25 °C. Hexane was used as a mobile phase. The chromatograms were processed using the Multichrom 1.5 program package. The chromatograph was calibrated using standard solutions of C_{60} in a toluene–hexane mixture in the range 0.003–0.05 mg ml^{-1}. The saturated solutions were diluted with tetrachloromethane in order to bring the C_{60} concentration within the calibration range. The accuracy of our measurements was 5%.

For converting weight concentrations into bulk concentrations, the densities of mixed solvents (*o*-dichlorobenzene–tetrachloromethane) were measured by a vibrating densimeter.

The measured solubilities of C_{60} in the *o*-dichlorobenzene–tetrachloromethane system are given in Table 1.

† Deceased.

Table 1 Solubility of C_{60} in *o*-dichlorobenzene–tetrachloromethane mixtures/mg ml^{-1}.

Mole fraction (*o*-$C_6H_4Cl_2$)	Temperature				
	298 K	308 K	318 K	328 K	338 K
0.000	*0.32*	*0.31*	*0.29*	*0.29*	*0.29*
0.103	*0.46*	*0.50*	*0.45*	*0.46*	*0.48*
0.306	*1.2*	*1.3*	*1.2*	*1.3*	*1.5*
0.500	*3.1*	*3.2*	*3.2*	*3.4*	*3.5*
0.691	*6.6*	*7.7*	*7.8*	*7.8*	7.1
0.900	*19*	*20*	12	10	11
1.000	*27*	23	15	12	13.5

The solubilities of C_{60} in pure CCl_4 and *o*-$C_6H_4Cl_2$ at 298 K are in good agreement with published data.[1] In pure *o*-$C_6H_4Cl_2$, we observed a decrease of the C_{60} solubility with temperature. However, the opposite results were obtained previously,[2,7,8] the increased solubility of C_{60} in *o*-$C_6H_4Cl_2$,[7] C_6H_6 and PhMe[2,8] with temperature. The most reliable data show that the solubility of C_{60} in toluene decreases with temperature.[6,9] Doome *et al.*[10] reported a maximum of C_{60} solubility in *o*-$C_6H_4Cl_2$ at 310 K. The maximum of the solubility–temperature relation was attributed to the aggregation of C_{60} molecules in the solution and the change of the composition of the solid phase. The same behaviour was observed in *n*-hexane,[6] *o*-xylene[9] and CS_2.[6,9] Note that the solubility values published[2,7,8] differ significantly from other values measured. The solubility of C_{60} in toluene and *o*-dichlorobenzene is given in Table 2 for comparison. The solubility of C_{60} in various solvents differs by several orders of magnitude. In many cases, there are deviations among the data determined by different authors. These deviations are due to problems related to experimental techniques[5] (HPLC analysis,[1,10] spectrophotometric analysis[3,9] and the evaporation of the solvent with the following weighing[2,8,11] of C_{60}). Different approaches have been made to increase the rate of dissolution and to reach an equilibrium in the system, such as the agitation of solutions for different periods of time,[1] sonication[11] and stirring during various times.[3,4,8,10]

We applied the following equation to analyse the dependence of the C_{60} solubility on the composition of a mixed solvent:

$$\ln (X/X_0) = KX_S, \quad (1)$$

where X_0 is the mole fraction of C_{60} in pure CCl_4 for each temperature; X is the mole fraction of C_{60} at a given solvent composition; X_S is the mole fraction of *o*-dichlorobenzene; K is an empirical constant.

Table 2 Solubility of C_{60} in toluene and *o*-dichlorobenzene at 298 K/mg ml^{-1}.

Toluene	0.54[8]	2.8,[1] 2.9,[9,11] 2.15[3]
o-Dichlorobenzene	7.11[7]	27,[1] 24.6,[11] 22.9[10]

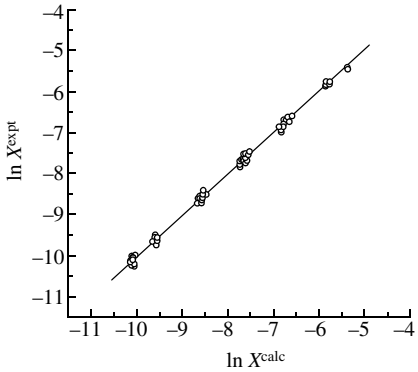

Figure 1 Experimental solubility of C_{60} fullerene in CCl_4–*o*-$C_6H_4Cl_2$ system *versus* solubility calculated by equation (4).

We found that $\ln X_0$ and K are linear functions of inverse temperature ($1/T$) and temperature (T), respectively (linearity was observed for italicised solubility values shown in Table 1). Therefore, we could apply isotherm equation (2), assuming that in a sufficiently small temperature interval, the change of heat capacity of solution may be neglected.

$$\ln X_0 = -\frac{\Delta_{soln}H^0}{RT} + \frac{\Delta_{soln}S^0}{R}. \quad (2)$$

After substitution of equation (2) into (1), and assuming that K is a linear function of temperature

$$K = K^{298.15} + \frac{\partial K}{\partial T}(T - 298.15), \quad (3)$$

the following expression for the dependence of solubility on solvent composition and temperature was obtained:

$$\ln X = -\frac{\Delta_{soln}H^0}{RT} + \frac{\Delta_{soln}S^0}{R} + K^{298.15}X_S + \frac{\partial K}{\partial T}(T - 298.15)X_S. \quad (4)$$

Experimental data were fitted to equation (4) using the least-squares analysis. We found that $\Delta_{soln}H^0$ is statistically insignificant (the standard error was about two times higher than the estimated $\Delta_{soln}H^0$ value). The calculated parameters of equation (4) are as follows: $\Delta_{soln}H^0 = 0$ kJ mol^{-1}; $\Delta_{soln}S^0 = -83.8\pm0.2$ J mol^{-1} K^{-1}; $K = 4.71\pm0.06$; $\partial K/\partial T = 0.0078\pm0.0027$ K^{-1}; determination coefficient, 0.987.

The dispersion of adequacy of experimental data calculated according to equation

$$S = \sqrt{\frac{\sum_{i=1}^{n}(\ln X^{expt} - \ln X^{calc})^2}{n(n-3)}} \quad (5)$$

was 0.165.

A correlation between experimental and calculated solubility values is shown in Figure 1. If $\Delta_{soln}H^0 << T\Delta_{soln}S^0$, the process of C_{60} solution in CCl_4 is controlled by the entropy factor. For a solution of C_{60} in *o*-dichlorobenzene, the following expression for the enthalpy of solution can be written:

$$\Delta_{soln}H^0 = RT^2X_S\frac{\partial K}{\partial T}. \quad (6)$$

For pure *o*-dichlorobenzene, $\Delta_{soln}H^0 = 5.8\pm2.2$ kJ mol^{-1} and $T\Delta_{soln}S^0 = 7.8$ kJ mol^{-1}. In this case, the solution process is controlled by both entropy and enthalpy factors. Note that the isotherm equation applied to describe the experimental data[10] resulted in the enthalpy of solution of a crystal solvate ($\Delta_{soln}H^0$) equal to 14.3 kJ mol^{-1}. On the other hand, it was reported[14] that *o*-dichlorobenzene can form a 1:2 solvate complex with C_{60} fullerene. $\Delta_{soln}H^0$ characterises a crystal solvate–solution equilibrium. Thus, $\Delta_{soln}H^0$ is the enthalpy of reaction of the solution of crystal solvates, and it can be expressed as

$$\Delta_{soln(s)}H^0 = \Delta_{soln(C_{60})}H^0 + \Delta_rH^0, \quad (7)$$

where $\Delta_{soln(C_{60})}H^0$ is the enthalpy of solution of C_{60} and Δ_rH is the enthalpy of incongruent melting of the solvate. The enthalpy of solution of C_{60} in *o*-dichlorobenzene and the enthalpy of incongruent melting of the solvate (C_{60}:2*o*-dichlorobenzene) were found to be -14.22 ± 0.20 and 18.5 ± 2.3 kJ mol^{-1}, respectively.[14] Thus, the enthalpy of crystal solvate solution is equal to 4.3 kJ mol^{-1}. It agrees well with the value obtained in this work.

This work was supported by the Russian Foundation for Basic Research (grant no. 05-03-32696).

References

1 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379.
2 T. M. Letcher, U. Domanska, A. Goldon and E. M. Mwenesongole, *S.-Afr. J. Chem.*, 1997, **50**, 51.
3 N. Sivaraman, R. Dhamodaran, I. Kaliappan, T. G. Srinivasan, P. R. Vasudeva Rao and C. K. Mathews, *J. Org. Chem.*, 1992, **57**, 6077.
4 D. Heymann, *Fullerene Sci. Technol.*, 1996, **4**, 509.
5 M. T. Beck and G. Mandi, *Fullerene Sci. Technol.*, 1997, **5**, 291.
6 R. S. Ruoff, R. Malhotra, D. L. Huestis, D. S. Tse and D. C. Lorents, *Nature*, 1993, **362**, 140.
7 U. Domanska and T. M. Letcher, *S.-Afr. Tydskr. Chem.*, 2000, 53.
8 T. M. Letcher and P. B. Crosby, U. Domanska, P. W. Fowler and A. C. Legon, *S.-Afr. Tydskr. Chem.*, 1993, **46**, 41.
9 X. Zhou, J. Liu, Z. Jin, Z. Gu, Y. Wu and Y. Sun, *Fullerene Sci. Technol.*, 1997, **5**, 285.
10 R. J. Doome, S. Dermaut, A. Fonseca, M. Hammida and J. B. Nagy, *Fullerene Sci. Technol.*, 1997, **5**, 1593.
11 W. A. Scrivens and J. M. Tour, *J. Chem. Soc, Chem. Commun.*, 1993, 1207.
12 V. N. Bezmelnitsyn, A. V. Eletskii and M. V. Okun, *Usp. Fiz.*, 1998, **168**, 1195 (*Phys. Usp.*, 1998, **41**, 1091).
13 Yu. V. Karyakin and I. I. Angelov, *Chistye khimicheskie veshchestva* (*Pure Chemicals*), Khimiya, Moscow, 1974, p. 408 (in Russian).
14 M. V. Korobov, A. L. Mirakyan, N. V. Avramenko, G. Olofsson, A. L. Smith and R. S. Ruoff, *J. Phys. Chem. B*, 1999, **103**, 1339.

Received: 2nd December 2004; Com. 04/2332

The English language edited by Valentin V. Makhlyarchuk, Moscow
Typeset by Sergei I. Ososkov, Moscow
Printed in the UK by Page Bros, Norwich