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THERMOCHEMISTRY OF FULLERENE C_{60} SOLUTIONS IN TOLUENE, *o*-XYLENE AND *o*-DICHLOROBENZENE

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Abstract

In hermetic highly sensitive calorimeter with an isothermal shell, the enthalpies of dissolution of fullerene C_{60} in toluene, *o*-xylene and *o*-dichlorobenzene were measured at temperatures of 288.15 K and 308.15 K at various concentrations of the dissolved substance. On the basis of the measured values and literature data, standard thermodynamic functions of the dissolution of C_{60} in the above mentioned solvents have been found at the indicated temperatures. The fact of the change in the sign of the dissolution enthalpy for all three systems under study at a transition to a temperature of 308.15 K has been revealed. A negative value of the dissolution entropy indicates the presence of a constant interaction in these liquid systems, which decreases sharply at 308.15 K

Keywords

Dissolution enthalpy, non-aqueous solvents, thermodynamic dissolution functions

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Introduction. Fullerenes belong among nanomaterials and are allotropic modification of carbon. Their molecules represent hollow particles formed by penta- and hexahedrons of carbon atoms linked by a covalent bond. The most common and well-studied is the C_{60} molecule (buckminsterfullerene), resembling a microscopic soccer ball whose surface consists of twenty hexagons and twelve pentagons. Each carbon atom at each vertex of each polygon belongs simultaneously to two hexagons and one pentagon [1, 2].

Fullerenes are becoming more and more widely used, for example, in the creation of new lubricants and new types of fuel, in the synthesis of diamond-like compounds of ultrahigh hardness, etc. Employing fullerene C_{60}, which is an effective antioxidant, shortly before exposure to γ-radiation or within thirty

minutes after the procedure, allows to reduce damage of internal organs by 50–60 %. In addition to the overall effect, C_{60} successfully protects kidney and some parts of nervous system against after-effects of irradiation. The possibility of drugs' fine tune by chemically modifying therapeutic compounds with fullerene C_{60} will allow in the perspective to create new types of therapy aimed at protecting well-defined organs and tissues [3].

Fullerene C_{60} is a low-solubility substance. Its solutions of acceptable concentrations in a number of organic solvents have unusual properties. One of these properties is having an extreme temperature dependence of solubility. Its maximum is being observed in the temperature range of 295–305 K [4–6]. Such a behavior of this compound during dissolution indicates a change in the sign of the enthalpy of dissolution, at least in the area of solutions close to saturation. And since the solubility of C_{60} in organic solvents is extremely small, a change in the sign of the dissolution enthalpy is likely to be observed at any concentrations. In this work toluene, *o*-xylene and *o*-dichlorobenzene were used as solvents for which the existence of an extreme temperature solubility dependence of the fullerene C_{60} was revealed and convincingly proved [5]. These solvents are high boiling compounds of an aromatic nature and belong to aprotic non-polar (toluene, *o*-xylene) and low-polar (*o*-dichlorobenzene) solvents.

Earlier [7], authors have determined dissolution enthalpies of fullerene C_{60} in these solvents at three or four solution concentrations and at a temperature of 298.15 K; their standard values were found as well. All determined values of dissolution enthalpies were exothermic. In this work, values of enthalpies of dissolution of fullerene C_{60} in toluene, *o*-dichlorobenzene and *o*-xylene in the area of dilute solutions at temperatures of 288.15 and 308.15 K are measured.

Experiment. A sample of fullerene C_{60} was singled out by researchers of the National Research Center "Kurchatov Institute" from graphite evaporation products [8]. After recrystallization from toluene, a chemical containing not less than 99.9 % (mass) of the basic substance has been obtained. The measurements of dissolution enthalpies were doing in a hermetic highly sensitive calorimeter with an isothermal shell [9], which had the following characteristics:

– thermometric sensitivity of the measuring bridge installation is about $8 \cdot 10^{-6}$ K;

– calorimetric sensitivity is equal to $8 \cdot 10^{-3}$ J;

– an accuracy of maintaining a constant temperature of an isothermal shell is about ± 0.003 K.

A semiconductor resistance thermometer was calibrated according to a reference thermometer and showed the following:

– resistance of the thermometer at the temperature of 288.15 K was 15 680 Ω, and at the temperature of 308.15 K it turned out to be 6 460 Ω;

– temperature coefficient of resistance at the temperature of 288.15 K was equal to 660 Ω/K, and at the temperature of 308.15 K its value was 190 Ω/K.

A thermal value of the calorimeter, filled with either 160 g of toluene, or 170 g of *o*-xylene, or 210 g of *o*-dichlorobenzene, was measured by the electrical way with a systematic error not more than 0.1 % in a series of five experiments. Upon that it was equal to, J/Ω: 0.926 ± 0.003 (toluene), 0.940 ± 0.003 (*o*-xylene), 0.880 ± 0.002 (*o*-dichlorobenzene) at the temperature of 288.15 K and 2.638 ± 0.003 (toluene), 2.644 ± 0.010 (*o*-xylene), 2.357 ± 0.010 (*o*-dichlorobenzene) at the temperature of 308.15 K. Concentrations of fullerene C_{60} solutions were ten thousandths fractions of molality. Such solutions were prepared by dissolving precisely weighed quantities of C_{60}, taken with the accuracy to 0.00005 g on electronic scales of Russian production. Upon that, the samples' weight was ranged from 0.01430 to 0.06375 g. The heat capacities of the solutions prepared in this manner, within the limits of error, coincide with the heat capacities of the solvents themselves. In this regard, the above meanings of the thermal value of the calorimeter filled with the solvent were used to calculate the amount of heat in experiments on measuring the enthalpies of dissolution of C_{60} in toluene, *o*-xylene and *o*-dichlorobenzene. Toluene, *o*-xylene and *o*-dichlorobenzene of the chemically pure grade produced by the company "ChemRar Group" have been used in this work. These solvents were being used without further purification. The reliability of the calorimetric installation was checked by measuring the dissolution enthalpy of $KCl_{(k)}$ in water at a temperature of 298.15 K and a molal concentration of the solution equal to 0.004 mol/kg. The resulting value was 17.32 ± 0.05 kJ/mol; within the error limits, it coincides with the most reliable literature data [10]. The heat of breaking the glass ampoule, measured in special experiments, was 0.000 ± 0.003 J. The summarized results of conducted measurements and calculations are presented in Table 1, which also contains brief information about the conditions for conducting calorimetric experiments:

– solution temperature T;

– molal concentration C_m of fullerene C_{60} in a solution;

– standard deviation of average result σ;

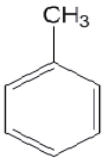
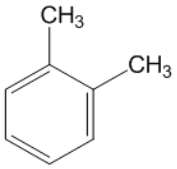
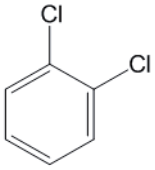
– Student t-test $t_{0.05}$;

– average value of the dissolution enthalpy $\Delta_{sol}H_a$.

For a temperature of 288.15 K, the value of the resistance thermometer is −15 000 Ω, for a temperature of 308.15 K the value is −6000 Ω.

Table 1

The average values of fullerene C_{60} dissolution enthalpies $\Delta_{sol}H_a$ in toluene, *o*-xylene and *o*-dichlorobenzene at temperatures 288.15 K and 308.15 K

Solvent	T, K	C_m, mol/kg	σ, kJ/mol	$\sigma t_{0.05}$, kJ/mol	$\Delta_{sol}H_a$, kJ/mol
Toluene 	288.15	0.00042	0.05	0.14	−9.73
		0.00028	0.03	0.08	−9.62
		0.00020	0.02	0.06	−9.53
	308.15	0.00052	0.03	0.08	6.82
		0.00037	0.02	0.06	6.92
		0.00016	0.02	0.06	6.98
o-Xylene 	288.15	0.00041	0.07	0.20	−10.00
		0.00028	0.07	0.20	−10.30
		0.00016	0.10	0.30	−10.80
	308.15	0.00039	0.04	0.11	6.94
		0.00025	0.02	0.06	6.81
		0.00013	0.02	0.06	6.71
o-Dichloro-benzene 	288.15	0.00058	0.10	0.30	−12.70
		0.00021	0.10	0.30	−13.00
		0.00011	0.10	0.30	−13.30
	308.15	0.00038	0.01	0.03	5.71
		0.00025	0.02	0.06	5.26
		0.00011	0.02	0.06	5.24

Results. The concentration dependence of fullerene C_{60} dissolution enthalpies in all studied solvents is being either insignificant or practically absent; when finding the values of standard enthalpies of C_{60} dissolution, in addition to the result of linear extrapolation of the above dependence to zero concentration, the enthalpy of dissolution at the minimum molal concentration was also taken into account. Founded in this work values of standard enthalpies of C_{60} dissolution in toluene, *o*-xylene and *o*-dichlorobenzene at temperatures of 288.15 K and 308.15 K are given in Table 2.

Table 2

Standard enthalpies of fullerene C_{60} dissolution $\Delta_{sol}H^0$ (kJ/mol) in toluene, *o*-xylene and *o*-dichlorobenzene at different temperatures

Solvent	$\Delta_{sol}H^0$ at temperatures, K	
	288.15	308.15
Toluene	−9.40 ± 0.15	7.05 ± 0.10
o-Xylene	−11.30 ± 0.30	6.60 ± 0.12
o-Dichlorobenzene	−13.50 ± 0.40	5.50 ± 0.10

Indeed, as can be seen from the Table 2 data for all three systems studied, there is a change in the sign of the standard dissolution enthalpy upon transition from a temperature of 288.15 K to a temperature of 308.15 K. In Table 3 the values of the standard thermodynamic characteristics of C_{60} dissolution in toluene, *o*-xylene, *o*-dichlorobenzene at temperatures of 288.15 K and 308.15 K are shown; for ease of comparison and convincing data obtained for the temperature of 298.15 K, the results of the authors from [7] are shown. A hypothetical one-molar solution with the properties of an infinitely diluted one is taken as the standard state. As can be seen from Table 3, for *o*-dichlorobenzene, values of the standard Gibbs energy $\Delta_{sol}G^0$ and dissolution entropy $\Delta_{sol}S^0$ at the temperature of 288.15 K are being absent: there are dashes instead. This is due to the very low solubility of fullerene C_{60} in this solvent at the indicated temperature and, for this reason, the presence in the literature of different data on its solubility. Therefore, the absence of their reliable values did not allow making calculations of the indicated thermodynamic characteristics.

Table 3

Standard Gibbs energy $\Delta_{sol}G^0$, enthalpy $\Delta_{sol}H^0$ and entropy $\Delta_{sol}S^0$ of fullerene C_{60} dissolution in toluene, *o*-xylene and *o*-dichlorobenzene at different temperatures

Solvent	*T*, K	$\Delta_{sol}G^0$, kJ/mol	$\Delta_{sol}H^0$, kJ/mol	$\Delta_{sol}S^0$, J/(mol·K)
Toluene	288.15	13.10 ± 0.30	−9.40 ± 0.15	−78.00 ± 1.00
	298.15	13.40 ± 0.30	−8.65 ± 0.10	−72.00 ± 1.00
	308.15	14.40 ± 0.30	7.05 ± 0.10	−24.00 ± 1.00
o-Xylene	288.15	12.30 ± 0.30	−11.30 ± 0.30	−82.00 ± 1.00
	298.15	11.70 ± 0.30	−10.00 ± 0.10	−73.00 ± 1.00
	308.15	12.40 ± 0.30	6.60 ± 0.12	−19.00 ± 1.00
o-Dichlorobenzene	288.15	–	−13.50 ± 0.40	–
	298.15	12.10 ± 0.30	−12.90 ± 0.12	−84.00 ± 1.00
	308.15	12.00 ± 0.30	5.05 ± 0.10	−23.00 ± 1.00

The first thing to note when analyzing the data of Table 3, these are the negative entropy values of the dissolution of C_{60} for all three systems studied. This feature indicates the presence in such liquid systems of a constantly existing interaction that compensates for an usual increase in entropy when solid substances dissolve. However, it is necessary to remember about the significant size of the fullerene C_{60} molecule. In this regard, the decrease in entropy in terms of 1 atom (1 mol of atoms) is small. The second thing that attracts attention when considering the numerical values of standard thermodynamic functions in the Table 3, this is a sharp decrease in the absolute value of the entropy of dissolution during the transition to the temperature of 308.15 K, due to changing the sign of the enthalpy of dissolution. The impression is being created that at a temperature of about 300 K the reason for the structurization of liquid systems, caused, for example, by some interaction, either disappears or sharply decreases.

Conclusion. The fact that the sign of the enthalpy of fullerene C_{60} dissolution in toluene, *o*-xylene and *o*-dichlorobenzene changes when changing the temperature from 288.15 K and 298.15 K to 308.15 K is experimentally established. The negative value of the entropy of dissolution in this case sharply decreases in absolute value, indicating a significant weakening of the existing interaction in liquid systems.

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