

FULLERITE IN ORGANIC MATRIX

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Introduction

Experimental investigations of fullerite C_{60} solubility in hexane, toluene, xylol and another organic solvents have shown the extremality of its temperature dependence (Fig. 1) [1-8].

The possible reason of such dependence is presented in the papers [2, 3], the authors of these presentations speculated that the structure of bonds in the flame of fullerene molecules changes with increase in temperature. This modify their chemical activity as well as their capacity for interaction with different amounts of solvent molecules.

As has already been mentioned [3], the fullerene molecules C_{60} are free to exist in the forms of three main resonance structures (Fig. 2). In this case the various types of crystal lattices correspond to the changing structures of bonds: simple cubic (sc) lattice corresponds to α -modification, body-centered cubic (bcc) to β -modification, face-centered cubic (fcc) – to γ -modification of fullerite. The phase transformations: $sc \rightarrow bcc \rightarrow fcc$ occur with increased temperature of fullerite [9, 10].

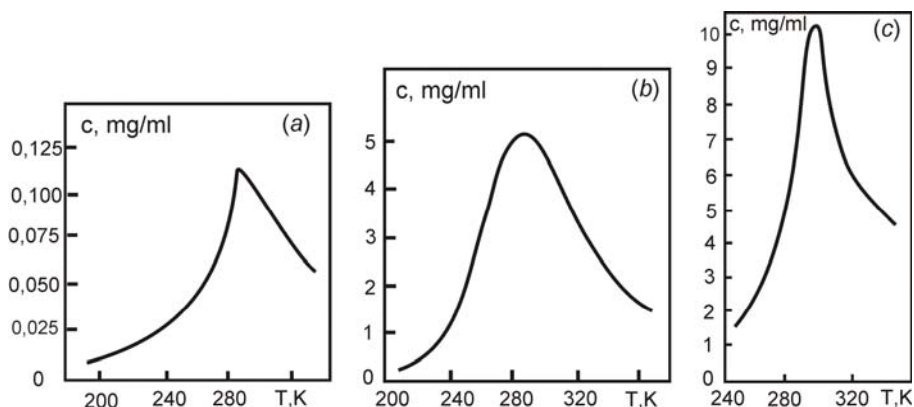


Fig. 1. The experimental plots of temperature dependence of fullerite C_{60} solubility in hexane (a), toluene (b), xylol (c) [1].

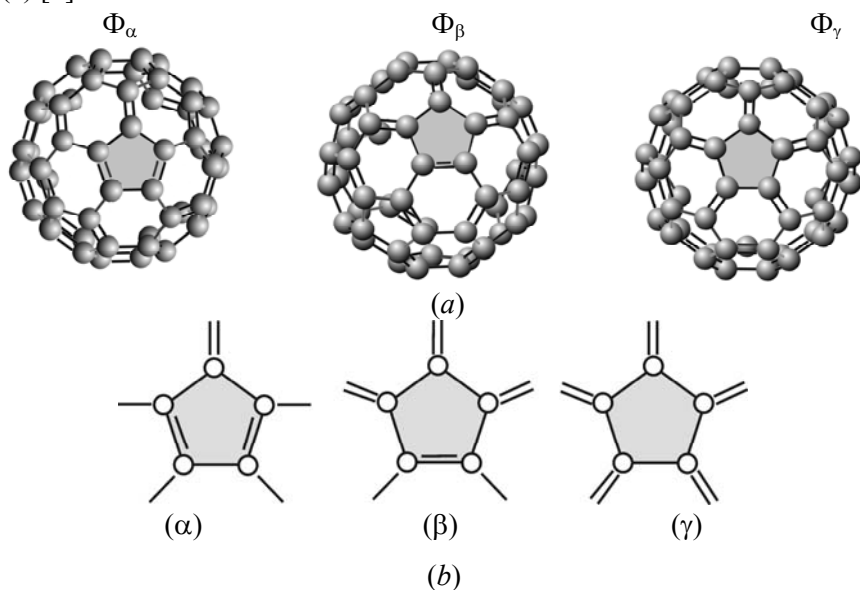


Fig. 2. The covalent resonance structures of fullerene $\Phi = C_{60}$ (Φ_α , Φ_β , Φ_γ) (a) with different quantity of double bonds in their pentatomic molecules (b): (α) – two double bonds in pentatomic molecule, (β) – one double bond in pentatomic molecule, (γ) – all bonds are single.

This paper presents the elaborated statistical theory of fullerite solubility in organic matrix taking into consideration the possibility of realization of different crystal structures of fullerite in different temperature intervals.

Theory

For solving a problem the free energy of the system is calculated by the formula

$$F_i = E_i - kT \ln G_i - kTN_i \ln \lambda_i, \quad i = \alpha, \beta, \gamma, \quad (1)$$

where E_i is internal configuration energy defined by the sum of energies of paired interaction between the nearest molecules of fullerite and solvent, G_i is thermodynamic probability of distribution of fullerene molecules and solvent molecules defined according to the rules of combinatorics, N_i is the number of fullerene molecules in crystal, λ_i is their activity, k is Boltzmann's constant, T is absolute temperature.

The calculation of free energy gives the following formula

$$F_i = -\frac{z_i}{2(N_i + N_s)}(N_i^2 v_{\phi\phi}^{(i)} + N_s^2 v_{ss}^{(i)} + 2N_i N_s v_{\phi s}^{(i)}) - kT[(N_i + N_s) \ln(N_i + N_s) - N_i \ln N_i - N_s \ln N_s - kTN_i \ln \lambda_i], \quad (2)$$

where N_i , N_p are the numbers of fullerene molecules Φ_i and solvent molecules S .

The equilibrium state of fullerite is determined from the conditions for minimum of free energy, that are easily found by the method of the indeterminate Lagrange factor. Substituting the free energy F_i into the conditions of free energy minimum, we receive the equation

$$c_i = [1 + \frac{1}{\lambda_i} \exp \frac{-z_i(v_{\phi p}^{(i)} - v_{pp}^{(i)} - c_i \omega_i)}{kT}]^{-1}. \quad (3)$$

The derived formula (3) determines the temperature dependence of fullerite solubility $c_i = c_i(T)$ in organic matrix. In formula (3)

$$\omega_i = 2v_{\phi p}^{(i)} - v_{\phi\phi}^{(i)} - v_{pp}^{(i)} \quad (4)$$

is the energy of mixing of each phase $i = \alpha, \beta, \gamma$. The form of dependence $c_i(T)$ is defined by energetic parameter

$$V_i = z_i(v_{\phi p}^{(i)} - v_{pp}^{(i)} - c_i \omega_i), \quad (5)$$

i.e. by the character of intermolecular interactions.

Interpretation of calculation results

Investigations have shown that the function $c_i = c_i(T)$ for each phase $i = \alpha, \beta, \gamma$ is monotonic. As this takes place, an increase or decrease of solubility of fullerite is determined by the sign of energy V_i (5). Over a wide range of temperatures, when phase transformations $sc \rightleftharpoons bcc \rightleftharpoons fcc$ take place and it is possible the change of sign of

energetic parameter V_i , the dependence $c_i = c_i(T)$ can be extremal.

By way of illustration let us consider the simple particular case, when the energy of mixing ω_i has a negligibly small quantity ($\omega_i \ll 1$). In this case formula (3) is simplified and has the form

$$c_i = \lambda_i \exp \frac{V_{i0}}{kT}, \quad i = \alpha, \beta, \gamma, \quad (6)$$

where $V_{i0} = z_i(v_{\phi p}^{(i0)} - v_{pp}^{(i0)})$. The energetic parameters $V_{i0} = V_{\alpha 0}, V_{\beta 0}, V_{\gamma 0}$ are evaluated using experimental data of Fig. 1 according to which the phases α, β, γ are realized respectively at the temperatures of $T = 240, 270, 290$ K.

The parameters are equal to $V_{\alpha 0} = -0,0022$ eV, $V_{\beta 0} = 0,032$ eV, $V_{\gamma 0} = 0,01$ eV. One can see from their values that the V_{i0} energy reverses sign in going from α to γ phase and $|V_{\alpha 0}| < |V_{\beta 0}| > |V_{\gamma 0}|$, i. e. the fullerite of phase β is bound to be of greatest solubility c_β in organic matrix.

Figure 3 shows the calculated plot of temperature dependence of fullerite solubility in organic medium. In two-phase regions the solubility of fullerite has been defined by the rule of line segments.

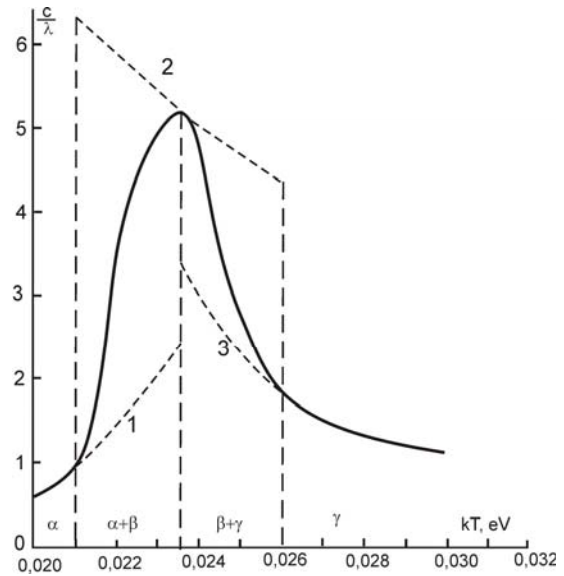


Fig. 3. The design plot for temperature dependence of fullerite solubility in organic matrix (a continuous curve). The α, β, γ phases correspond to the formation of fullerite in different temperature intervals with sc, bcc, fcc lattices. The dotted curve determines the fullerite solubility for uncombined α, β, γ phases.

Conclusions

The comparison of experimental (Fig. 1) and theoretical (Fig. 3) plots shows the identity of their form. The presence of maximum on the plot

of temperature dependence of fullerite solubility in organic matrix is evident and this maximum fall on the temperature interval that corresponds to the formation of fullerite of β -modification.

This fact permits a hope that the conceived idea about the existence of three stable isomers of fullerene molecules C_{60} is realistic and these isomers differ by activity and stability temperature, defined by the processes of change of interatomic bonds from intramolecular to extramolecular.

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