Solubility of Light Fullerenes in Vegetable Oils

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Abstract—Polythermal (in the temperature range 0–80°C) solubility of light fullerenes (C_{60} and C_{70}), and also of fullerene mixtures (65% C_{60}, 34% C_{70}, and 1% C_{76-90}) in vegetable oils (of unrefined and refined sunflower, corn, olive, linen, apricot, grape, cedar, and walnut) was studied; the corresponding solubility polytherms are given and characterized.

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In spite of the fact that the solubility of light fullerenes in a wide set of solvents was multiply studied, still the corresponding published data are obviously insufficient for the following reasons.

The scarcity of the data on the solubility of the second light fullerene C_{70} in binary systems due presumably to its considerably lesser accessibility and higher price than those of the first light fullerene C_{60}. For comparison: at 25°C (sometimes at 20°C) the solubility of C_{60} has been measured in 150 solvents, whereas the solubility of C_{70}, only in 20 solvents.

A number of works are devoted to the study of the solubility of the both light fullerenes in polythermal conditions. The solubility of C_{60} fullerene has been studied in the following solvents: hexane [1–3], tetralin [8], carbon disulfide [1, 2, 5], perchloromethane [6, 7], and butylamine [2, 4]; in some aromatic solvents: benzene [2–4], toluene [1–3, 5–7], o-xylene [2, 3, 5, 9], o-di chlorobenzene [1–6, 8], 1,2,4-trichlorobenzene [2, 4], 1,3-diphenylacetone [8], thiophene [2, 4], tetrahydrothiophene [2, 4], tetrahydrofuran [2, 4], higher isomeric carboxylic acids [10], monobasic carboxylic acids of a normal structure [11–14], and olive-kernel oil [15]. The solubility of C_{70} fullerene has been studied in the following solvents: tetralin [8], perchloromethane [3, 5], aromatic solvents (toluene [3, 5], o-xylene [3, 5], o-dichlorobenzene [8], 1,3-diphenylacetone [8]), monobasic carboxylic acids of a normal structure [11–14], and monohydroxy alcohols of a

normal structure [17]. It is necessary to note that data on the solubility of both fullerenes together in the same solvent are practically absent from the literature. In [9] the solubility in the ternary system C_{60}–C_{70}–o-xylene was studied at −20, 25, and 80°C, and in [16] the same system was studied at 25°C. Aside from it, in [13] the solubility of the standard fullerene mixtures (C_{60} 60, C_{70} 39, C_{76-90} 1 wt %) was studied in butyric and oenanthylic acids in the temperature range of 20–80°C.

A similar pattern appears also for the solubility diagrams in the systems individual fullerene-mixed solvent. In [10] the solubility of light fullerenes in a mixture of higher isomeric carboxylic acids was studied under polythermal conditions, and in [15] the C_{60} fullerene solubility in olive oil, which represents, as is known, a multicomponent mixture of triglycerides of various fatty carboxylic acids, was studied at 25°C.

The solubility of light fullerenes in various fats and oils was studied also insufficiently. Apart from the work [15], in which the C_{60} fullerene solubility of ~4–6 g l^{-1} in olive oil was determined as a function of temperature, we can note only several Russian Federation patents of 2001–2006 [18–22] on the solubility of light fullerenes in various fats of a vegetative and animal origins, which was estimated exclusively on a qualitative level, both true and microhetero-geneous, cluster and colloidal, solutions of fullerene being considered.

In the present work we studied the solubility of light fullerenes, individual C_{60} and C_{70}, and also standard fullerene mixtures (C_{60} 65, C_{70} 34, and C_{76-90} 1 wt %) in liquid natural vegetable oils (unrefined and refined sunflower, corn, olive, linen, apricot, grape, cedar, and walnut) in the temperature range 0–80°C.

As is known, fats (oils) are substances of animal, vegetative or microbial origin, mainly (up to 98 wt %) consisting of triglycerides-full ethers of glycerin and fatty acids. In addition they contain di- and mono-glycerides (1–3 wt %), phospholipids, glycollipids, diol lipids (0.5–3 wt %), free fatty acids, stearines and their ethers (0.05–1.7 wt %), and also coloring substances, vitamins A, D, E, and K, polyphenols, and their ethers (in trace amounts). Chemical properties of fats (oils) are mainly defined by the chain length, the unsaturation degree of fatty acids, and by their location in triglycerides. As a rule, fats (oils) include unbranched fatty acids with an even number of carbon atoms (4–26), both saturated and unsaturated, including polyunsaturated. In vegetable fats (oils) the main part of unsaturated acids is contained in β-positions of triglycerides, and at high content of unsaturated acids, also in α-positions, whereas saturated acids are mainly contained in β-positions of triglycerides [23]. The compositions of the main natural vegetable oils (in terms of fatty acids) used in this work as solvents are presented in Table 1 (because of the data absence apricot oil is replaced by peach oil).

The study of the solubility of light fullerenes in liquid natural vegetable oils is an actual problem for several reasons. Fullerenes are rather readily soluble in these natural solvents in the specified temperature range - from tenths up to unities of grams of fullerenes per a liter of a solution (Table 2). Fullerenes and natural vegetable oils form absolutely transparent true solutions stable in time. Such solutions are completely harmless and compatible with human and animal organisms when they are prepared directly at the extraction of a fullerenes mixture from fullerene soot by natural vegetable oils, i.e. when they practically do not contain any harmful admixtures.

Standard fullerenes obtained as a rule from solutions in aromatic solvents (toluene, xylenes, di-chlorobenzenes, etc.) inevitably contain remains of these solvents. Even after an hours-long high-temperature (200–250°C) drying in sufficiently high vacuum (0.01 mm Hg) the remaining content of solvents is from thousandth up to hundredth parts of

wt %. The alternative complete removal of admixed solvents can be reached probably only by a vacuum high-temperature sublimation of fullerene at very low residual pressures ($<10^{-5}$ mm Hg). The experiment shows that such process is rather expensive and labor-consuming, and, therefore, for example, the price for so-called "sublimated fullerene C_{60}" free from admixed solvents is 2–4 times higher than the price for "ordinary" fullerene C_{60} obtained by the standard procedure of drying in a vacuum box.

Fullerene solutions in oil show expressed antibactericidal and antioxidant properties, absorb free radicals from condensed phases, in which they are present, ion radicals, and also photons in the UV spectral range [24, 25] that undoubtedly can be used in practice.

Temperature dependence of the solubility of individual fullerenes (C_{60} and C_{70}), and also of the fullerene mixture (C_{70} 34, C_{60} 65, C_{76-90} 1 wt %) was studied by the isothermal saturation method. Concentrations after each stage of saturation with C_{60} and C_{70} fullerenes and the mixture were determined by the spectrophotometric method. Solvent contents in crystal solvates of fullerenes were experimentally determined by the gravimetrical method.

Electron absorption spectra of the C_{60}, C_{70} fullerene mixture (C_{70} 34, C_{60} 65, C_{76-90} 1 wt %) in olive oil are presented in Fig. 1 as an example. Almost complete absence of solvatochromic effects is observed (no sharp change of the optical spectrum on a minor variation of solution concentration or solvent composition is observed) that allows us to use quite reliably empirical formulas deduced in [26] for the calculation of fullerenes concentrations.

As to possible composition of crystal solvates and their dissociation temperatures in the systems light fullerenes–natural oils, in our opinion it is meaningful to carry the following consideration. We neglect the presence of di- and monoglycerides, phospholipids, glycolipids, diol lipids, free fatty acids, stearines, their ethers, coloring substances, vitamins, polyphenols, their ethers, and other substances which are present in trace amounts in the oil under discussion, i.e. we shall consider oil consisting exclusively of triglycerides. Such assumption is rather natural, as the content of these latter in vegetable oils is actually high and reaches 98 wt %. If the oil consists of a unique triglyceride, let it be of the mixed composition TG ≡ $R_1(CO)OCH_2−CH(COOR_2)−CH_2O(CO)R_3$, such oil

Table 1. Averaged composition of vegetable fats (in terms of the content of fatty acids)[a]

Vegetable oil type	Content of fatty acids, wt %			
	lauric	myristic	palmitic	palmitoleic
Corn	<0.3	<0.3	9.0–14	<0.5
Grape	–	<0.2	5.6–7.6	<0.3
Olive	–	–	7.0–20.0	0.3–3.5
Peachy	–	<0.1	<3.0	–
Sunflower	–	<0.2	5.0–7.6	<0.3
Cedar	–	–	3.0–3.9	–
Walnut	–	–	8.0	–
Linseed	–	–	7.0	–

Vegetable oil type	Content of fatty acids, wt %			
	stearinic	oleic	linoleic	linolenic
Corn	0.5–4.0	24–42	34–62	–
Grape	2.7–6.5	14.6–39.4	18.3–74.0	–
Olive	1.5–4.3	56.0–86.0	3.3–20.0	0.4–1.5
Peachy	10.0–15.0	73.3–85.0	5.0–16.4	–
Sunflower	2.7–5.5	14.0–39.4	48.3–77.0	<0.3
Cedar	3.4–4.1	22.1–26.0	36.99–69.0	18.0–24.3
Walnut	2.0	20	56	14
Linseed	3.0	25	12	50

Vegetable oil type	Content of fatty acids, wt %			
	arachidonic	gondoic	eicosapentaenoic	behenic
Corn	<1.0	<0.5	–	<0.5
Grape	0.2–0.4	<0.2	–	0.5–1.3
Olive	0.2–1.6	0.2–0.5	–	–
Peachy	–	–	–	–
Sunflower	<0.5	<0.3	–	0.3–1.5
Cedar	<0.3	0.8–1.3	<0.4	–
Walnut	–	–	–	–
Linseed	–	–	–	–

Vegetable oil type	Content of fatty acids, wt %	
	erucidic	lignoceric
Corn	<0.5	–
Grape	0.5–1.3	<0.2
Olive	–	–
Peachy	–	–
Sunflower	0.3–1.5	–
Cedar	–	–
Walnut	–	–
Linseed	–	–

[a] A dash denotes either a very low value or the fact that the value was not determined.

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Table 2. Solubility of light fullerenes in vegetable oils

Solvent	C_{60} solubility, g l^{-1}				
	0°C	20°C	40°C	60°C	80°C
"Stavropol'e" (unrefined sunflower) oil	0.294	0.451	0.727	0.708	0.638
"Zlato" (refined sunflower) oil	0.299	0.377	0.456	0.570	0.697
"Milora" (corn) oil	0.196	0.609	0.846	0.945	1.319
Walnut oil	0.269	0.485	0.694	0.718	1.017
Olive oil	0.264	0.470	0.751	0.858	1.206
Linseed oil	0.229	0.513	0.639	0.717	1.033
Cedar nut oil	0.323	0.485	0.818	1.053	1.099
Grape oil	0.327	0.371	0.663	0.748	0.897
Apricot oil	0.372	0.509	0.702	0.799	0.958
	C_{70} solubility, g l^{-1}				
"Stavropol'e" (unrefined sunflower) oil	0.504	1.827	2.647	2.872	3.213
"Zlato" (refined sunflower) oil	0.303	1.289	1.668	2.996	3.261
"Milora" (corn) oil	0.506	1.957	2.963	3.404	4.286
Walnut oil	0.315	1.390	1.829	2.650	2.837
Olive oil	0.402	0.756	1.286	2.735	3.278
Linseed oil	0.505	1.198	1.639	2.118	2.773
Cedar nut oil	0.378	0.757	1.512	2.020	2.710
Grape oil	0.632	0.947	1.578	2.207	2.838
Apricot oil	0.378	1.009	2.208	2.772	3.090
	$C_{60} + C_{70}$ (65% C_{60}, 34% C_{70}, 1% C_{76-90}) solubility, g l^{-1} [a]				
"Stavropol'e" (unrefined sunflower) oil	1.831	2.234	2.068	1.839	1.612
	0.898	1.045	1.361	1.843	2.320
"Zlato" (refined sunflower) oil	1.828	2.284	2.510	2.663	2.864
	1.279	1.456	1.731	1.825	2.199
"Milora" (corn) oil	1.949	2.294	2.746	2.619	2.735
	1.209	1.201	1.346	1.664	1.976
Walnut oil	1.378	2.127	2.156	2.264	2.340
	0.752	0.890	1.362	1.517	1.546
Olive oil	1.239	2.900	2.224	2.135	2.150
	0.913	1.123	1.518	1.747	1.999
Linseed oil	1.733	2.097	2.067	1.987	1.923
	0.900	1.117	1.207	1.524	1.778
Cedar nut oil	1.711	2.026	2.479	2.484	2.607
	1.370	1.681	1.826	2.079	2.294
Grape oil	1.693	1.801	2.092	2.263	2.224
	1.059	1.214	1.301	1.517	1.675
Apricot oil	1.437	1.791	1.905	2.086	2.097
	0.908	1.056	1.463	1.487	1.553

[a] Upper value relates to the C_{60} solubility, lower relates to the C_{70} solubility from the fullerene mixture.

would have a well-defined composition of a crystal solvate, for example, fullerene C_{60} KS$\equiv C_{60}N$(TG) (here N is the solvate number in this crystal solvate), and a well-defined temperature of dissociation, for example, by the scheme $C_{60}N(TG)_{(s)} \rightarrow C_{60(s)} + N(TG)_{(l)}$. However it is impossible to assign such unique triglyceride to any of oils, as, first, by oils contain five and more various fatty acids (Table 1), and it is principally impossible "to pack" them into one triglyceride, and, secondly, mole ratios of acids in such unique triglyceride should be either 1:1:1 or 1:2, which is by no means observed for real natural oils. Thus, it is necessary to accept that the oils represent a multicomponent mixture of different triglycerides: $TG_1 + TG_2 + \ldots + TG_m$ (m is the number of various triglycerides in the given oil). Owing to structural and chemical closeness, all such triglycerides should readily substitute each other in the crystal solvate structure, for example, of the following composition: $KS\equiv C_{60}(TG_1)_N (TG_2)_N \ldots (TG_{m-1})_N (TG_m)_{N-N-N-\ldots N}$, and from general considerations the number of triglycerides in a crystal solvate molecule should be half-integer or a minor even ($N = 1/2$ or 1, or 2, or 4) [1–15]. Analogous pattern should be also observed for crystal solvates of solid solutions of light fullerenes $KS\equiv(C_{60})_x(C_{70})_{1-x}(TG_1)_N (TG_2)_N \ldots (TG_{m-1})_N (TG_m)_{N-N-N-\ldots N}$.

The obtained polytherms of fullerenes C_{60} and C_{70} solubility in vegetable oils in the temperature range 0–80°C are presented in Figs. 2, 3 and in Table 2.

It is seen from Figs. 2 and 3 that the solubility increases with increasing temperature from 0 up to 80°C for both fullerenes C_{60} and C_{70} in all natural oils (by a factor of 2–3 for the C_{60} fullerene and 5–10 for the C_{70} fullerene); the solubility of the C_{60} fullerene in a specified natural oil is always higher than the solubility of the C_{70} fullerene (as a rule, by a factor of 1.5–2.0 at 0°C and 3–5 at 80°C); the highest solubility for both fullerenes is observed at high temperatures for corn oil.

Polytherms of the $C_{60} + C_{70}$ sum of fullerenes solubility in natural oils from the fullerene mixture (C_{60} 65, C_{70} 34, $C_{76} + C_{78} + C_{84} + C_{90} \ldots 1$ wt %) are presented in Fig. 4 and Table 2. (content of the highest fullerenes C_{76-90} in the specified fullerene mixture was neglected in this study). It is seen from Fig. 4 that the solubility of the $C_{60} + C_{70}$ sum of fullerenes as a whole also monotonically increases by a factor of 2–3 up to 3–5 g l^{-1} depending on natural oil type as temperature increases from 0 up to 80°C.
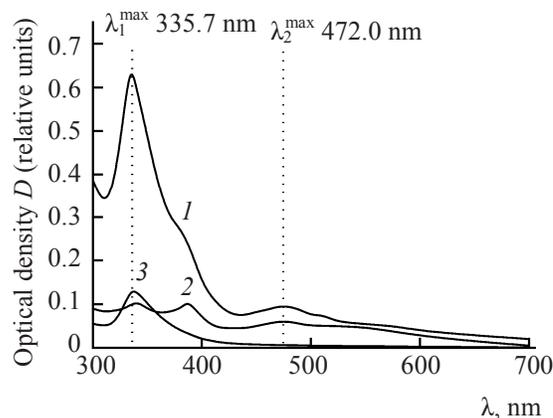

Fig. 1. Absorption spectrum of light fullerenes in olive oil: (*1*) fullerene mixture (C_{60} 65, C_{70} 34, $C_{76} + C_{78} + C_{84} + C_{90} \ldots$ - 1 wt %), (*2*) fullerene C_{70} (99 wt %), and (*3*) fullerene C_{60} (99.9 wt %).
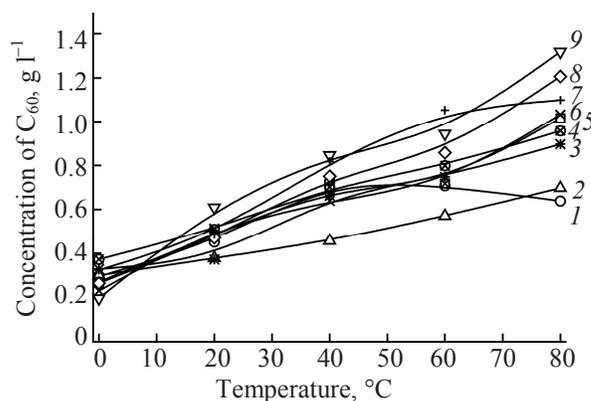

Fig. 2. Polytherm of C_{60} fullerene solubility in vegetable oils in the temperature range 0–80°C. (*1*) "Stavropol'e" unrefined sunflower oil, (*2*) "Zlato" refined sunflower oil, (*3*) linseed oil, (*4*) apricot oil, (*5*) walnut oil, (*6*) grape oil, (*7*) cedar oil, (*8*) olive oil, and (*9*) "Milora" corn oil.
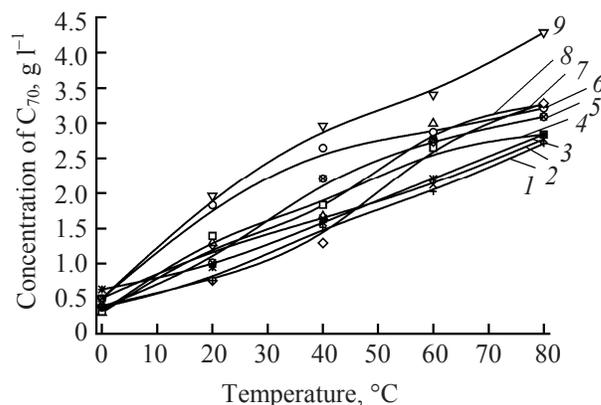

Fig. 3. Polytherm of C_{70} fullerene solubility in vegetable oils in the temperature range 0–80°C. (*1*) cedar oil, (*2*) linseed oil, (*3*) grape oil, (*4*) walnut oil, (*5*) apricot oil, (*6*) "Stavropol'e" unrefined sunflower oil, (*7*) olive oil, (*8*) "Zlato" refined sunflower oil, and (*9*) "Milora" corn oil.
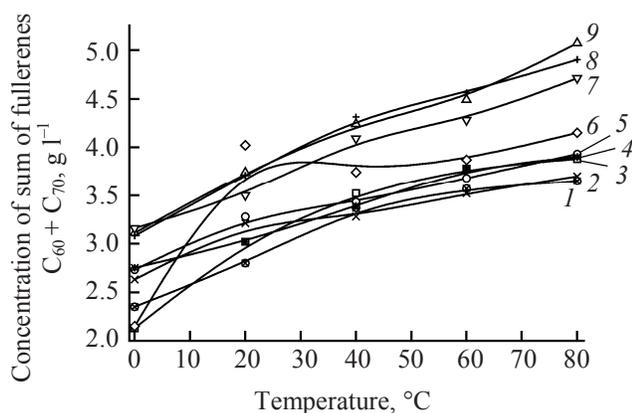
Fig. 4. Polytherm of the fullerene mixture (C_{60} 65, C_{70} 34, $C_{76} + C_{78} + C_{84} + C_{90}$ … 1 wt %) solubility in vegetable oils in the temperature range 0–80°C. (*1*) Apricot oil, (*2*) linseed oil, (*3*) walnut oil, (*4*) grape oil, (*5*) "Stavropol'e" unrefined sunflower oil, (*6*) olive oil, (*7*) "Milora" corn oil (*8*) cedar oil, and (*9*) "Zlato" refined sunflower oil.
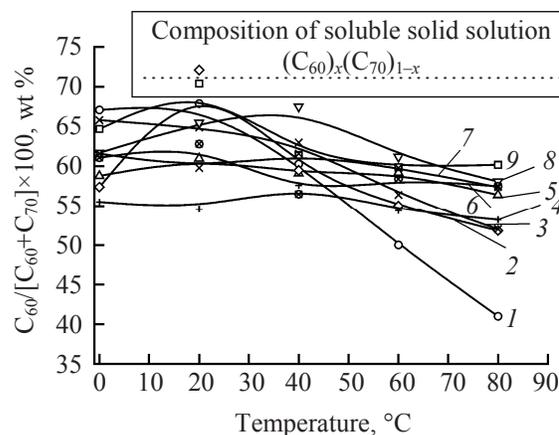

Fig. 5. Content of C_{60} fullerene in $C_{60} + C_{70}$ mixture in a liquid solution at the extraction of 10 mg of the fullerene mixture (C_{60} 65, C_{70} 34, $C_{76} + C_{78} + C_{84} + C_{90}$ … 1 wt %) by 10 ml of a vegetable oil as a function of temperature [content of the highest fullerenes ($C_{76} + C_{78} + C_{84} + C_{90}$ … 1 wt %) was neglected]. (*1*) "Stavropol'e" unrefined sunflower oil, (*2*) olive oil, (*3*) linseed oil, (*4*) walnut oil, (*5*) "Zlato" refined sunflower oil, (*6*) apricot oil, (*7*) grape oil, (*8*) "Milora" corn oil, and (*9*) walnut oil.

Content of the C_{60} fullerene in the $C_{60} + C_{70}$ mixture in a liquid solution at the extraction of 10 mg of the fullerene mixture (C_{60} 65, C_{70} 34, $C_{76} + C_{78} + C_{84} + C_{90}$ … 1 wt %) by 10 ml of a vegetable oil as a function of temperature is presented in Fig. 5. It is seen from Fig. 5 that at the low-temperature (0–40°C) extraction the liquid solution is not practically enriched as compared to the primary solid mixture of fullerene, whereas at high temperatures (60–80°C) the liquid phase is enriched in more polarizable C_{70} fullerene, the maximal enrichment being observed at the extraction with the unrefined sunflower oil.

The analysis of crystal solvates formed at rather low temperatures ($T \le 40$°C) (by the example of olive oil) has shown that the weight loss of a crystal solvate sample after multiple washing with ethanol and subsequent drying in a vacuum drying case is $\Delta m \approx$ 18±5 wt %. The average molecular weight of the mixed triglycerides forming the olive oil body is $M \approx$ 885±15 atomic units. It was supposed in the calculation that one averaged triglyceride molecule contained 2.10 acid residuals of oleic acid $CH_3(CH_2)_7\cdot$ $CH=CH(CH_2)_7COOH$, 0.45 acid residuals of palmitic acid $CH_3(CH_2)_{14}COOH$, and 0.45 acid residuals of linoleic acid $CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$ (Table 1). Then the elementary calculation allows to find the averaged composition of the crystal solvate $KS \equiv C_{60}$ (0.17±0.05)TG, where TG is the conventional

averaged molecule of an olive oil triglyceride. Thus, one acid residual in a triglyceride keeps two fullerene C_{60} molecules. Similar results are also obtained for conventional crystal solvates of C_{60} and other oils, and also for conventional C_{70} crystal solvates and solid solutions based on C_{60} and C_{70} crystal solvates. Therefore, light fullerenes and solid solutions on their basis form crystal solvates with natural vegetable oils with a rather low content of a solvent (compared to others crystal solvates) stable at temperatures close to room temperature.

EXPERIMENTAL

In the studies we used C_{60} fullerene of 99.9 wt % purity with the main assignable C_{70} fullerene admixture (~0.1 wt %), C_{70} fullerene of 99.4 wt % purity with the main assignable $C_{60} + C_{76-90}$ admixtures (0.6 wt %), and also a fullerene mixture consisting of 34 C_{70}, 65 C_{60}, and 1% C_{76-90} of CJSC ILIP (St. Petersburg) production, analytical-grade *o*-xylene , and also vegetable oils and sunflower (unrefined and refined), corn, olive, linen, apricot, grape, cedar, and walnut oils fitting the set storage time. The temperature dependences of the solubility of individual fullerenes (C_{60}, C_{70}), and also fullerene mixtures (34 C_{70} 34, C_{60} 65, C_{76-90} 1 wt %) were experimentally studied by the isothermal saturation method. Originally solutions of C_{60} and C_{70} and the fullerene mixture in

oils (in all cases a considerable excess of fullerenes of 100 mg of fullerenes per 10 ml of an oil) were prepared. Then the obtained heterogeneous systems were exposed to saturation in the temperature range of 0-80°C in a thermostatic shaker (temperature control accuracy of ±0.05°C) within 8 h at each temperature. After each stage of saturation with C_{60} and C_{70} fullerenes and with a mixture we determined concentrations by the spectrophotometric method on a SPECORD M-40 double-beam spectrophotometer at wavelengths of 335.7 and 472.0 nm. The accuracy of the wavelength fixing $\Delta\lambda$ was ±0.5 nm, the photometric accuracy ΔD ±0.005 rel. units (at a spectrophotometric cell width l of 1 cm). Concentrations were calculated on the basis of empirical formulas, which have been deduced in [26] for solutions of fullerene mixtures.

$$c(C_{60}) = 13.1[D_{335.7} - 1.81D_{472.0}], \quad (1)$$

$$c(C_{70}) = 42.5[D_{472.0} - 0.0081D_{335.7}]. \quad (2)$$

Here $c(c_i)$ is the fullerene concentration c_i in a solution in mg l^{-1}, D_i is an optical density of a solution on a wavelength $\lambda = i$ nm at $l = 1$ cm. The concentration of higher fullerenes c_i ($i \geq 76$) in the solution was neglected in these determinations. The total error in the determination of concentrations of light fullerenes c_i ($i = 60, 70$) was no more than 5%. An additional analysis was carried out by the liquid chromatography method on a LYUMAKHROM chromatograph (LUMEX corporation, St. Petersburg) following the procedure [27]. The detecting was carried out by the spectrophotometric method, by light absorption on a wavelength of 254 nm from mixed methylene chloride–acetonitrile solutions at the total concentration of previously diluted solutions of the order of units of mg of fullerenes/L. The relative error in the determination of concentrations of light fullerene c_i ($i = 60, 70$) was no more than 3%.

The content of a solvent in possible crystal solvates (by the example of systems with olive oil) was determined as follows: a solid phase freshly precipitated from a solution of fullerenes in olive oil was twice washed with ethanol, then dried in air at 20–25°C within 30 min, and weighed. After that the solid phase was multiply washed in a Soxhlet apparatus by ethanol (at 78°C, 1 atm), dried in a vacuum (0.1 mm Hg) at 200°C within 1 h, and then weighed for the second time. The content of olive oil components in an initial crystal solvate (or in a solid solution of fullerenes based on it) was determined from the change of the phase weight.

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