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Solubility of Light Fullerenes in Styrene

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This Article presents data on the solubility of fullerenes in binary $C_{60} + C_6H_5CH{=}CH_2$ and $C_{70} + C_6H_5CH{=}CH_2$ systems within the temperature range from (15 to 80) °C and the solubility of fullerenes along with their distribution between liquid and solid phases in the ternary $C_{60} + C_{70} + C_6H_5CH{=}CH_2$ system at temperatures of (−15, 0, and 25) °C. The solubility polytherms for the said binary systems and isotherms for the said ternary system are discussed; compositions of equilibrium solid phases are determined.

Introduction

It is well known that fullerene solubility investigations are important for understanding such processes as crystallization and extraction for fullerene separation from soot and fullerenes mixture, chromatographic and prechromatographic separation of fullerenes mixture, research of homogeneous chemical reactions with fullerene participation, and so on. However, there is an apparent shortage of data on the solubility of light fullerenes C_{60} and C_{70} as well as of heavier fullerenes. Isothermal solubility of C_{60} and C_{70} fullerenes has been measured mainly at 25 °C in approximately 150 and 20 solvents, correspondingly. The reason that the number of solvents for the C_{70} fullerene is so limited is likely to be connected to the fact that the C_{70} fullerene is comparatively more difficult to access. Polythermal solubility of the C_{60} fullerene was investigated for a still narrower number of solvents: *n*-hexane,[1−3] tetraline,[8] carbon bisulphide,[1,2,5] carbon tetrachloride,[6,7] *n*-butylamine,[2,4] benzene,[2−4] toluene,[1−3,5−7] *o*-xylene,[2,3,5,9] *o*-dichlorobenzene,[1−6,8] 1,2,4-trichlorbenzene,[2,4] 1,3-diphenylacetone,[8] thiophene,[2,4] tetrahydrothiophene,[2,4] tetrahydrofurane,[2,4] higher isomeric carbon acids,[10] monobasic carbon acids with normal structure,[11,12] and olive oil.[13] Polythermal solubility of the C_{70} fullerene was studied in the following solvents: tetraline,[8] carbon tetrachloride,[3,5] toluene,[3,5] *o*-xylene,[3,5] *o*-dichlorobenzene,[8] 1,3-diphenylacetone,[8] and monobasic carbon acids of normal structure.[11,12]

Surprisingly, it is very difficult to find any data concerning the simultaneous solubility of C_{60} and C_{70} fullerenes in the same solvent and the solubility of particular fullerenes in the mixed solvents. We could find only two papers concerning this problem.[9,14] Thus, in ref 9, the solubility in ternary system $C_{60} + C_{70} +$ *o*-xylene was investigated at temperatures of (−20, 25, and 80) °C. A phase diagram of the system enabled the authors to use it for prechromatographic separation of industrial fullerene mixture. Ref 14 is devoted to the solubility of the same system at 25 °C only.

The following reasons have driven us to choose binary and ternary systems that contain light fullerenes C_{60} and C_{70} and styrene as a solvent as an object for our investigation. It is known that an admixture of both fullerenes and fullerene mixture to a liquid/melt monomer followed by polymerization can form a fullerene-containing copolymer in the case of the formation of a true solution/melt. New polymeric materials that have unique or at least improved commercial characteristics can be prepared in this way.[15] For example, a polymerization of polyamide-6 with admixtures of light fullerenes is described in ref 15. Another example of solvent is styrene. It readily forms true solutions with light fullerenes at room temperature. Therefore, by choosing styrene as a monomer component, one gets a chance to obtain a large number of new copolymer based on polyamide-6, butadiene−styrene rubber, ABC plastics, and so on.

Styrene is one of a few monomers that is capable of copolymerization and at the same time is allowed to reach a high true solubility of light fullerenes—up to 10 $g \cdot dm^{-3}$. Such a solubility level is at least two orders of magnitude higher than fullerene solubility in polyamide-6.

The temperature was chosen to range from (−15 to 80) °C because at temperatures higher than 80 °C, a spontaneous polymerization of styrene takes place in fullerene−styrene systems (during about 12 h). The polymerization reveals itself in visible stiffening of the solution (or the melt) and makes the experiment on the solubility determination incorrect. It is notable that polymerization occurs despite the fact that light fullerenes are generally effective inhibitors of polymerization.

Materials and Methods

We used the C_{60} fullerene of purity 99.9 % wt and the C_{70} fullerene of purity 99.5 % wt (purchased from ILIP, St. Petersburg) with controllable principal admixtures C_{70} in C_{60} and C_{60} in C_{70} of (0.1 and 0.5) % wt, correspondingly. The composition of standard fullerene mixture (purchased from ILIP, St. Petersburg) was 60 % wt of C_{60}, 39 % wt of C_{70}, and 1 % wt of $C_{76}−C_{90}$. The other reagents used were reagent grade *o*-xylene and styrene stabilized with hydroquinone (purchased from Vecton, St. Petersburg).

The concentrations of C_{60} and C_{70} fullerenes in liquid styrene were measured with the aid of spectrophotometric technique (using the double-beam spectrophotometer Specord M40 made in Germany, Karl Zeiss) at characteristic wavelengths of (335 and 472) nm corresponding to the maximum absorbances that are stable relative to a solvent change. The accuracy of wavelength maintenance was ± 0.5 nm, the photometric

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Table 1. Light Fullerene Solubility in Styrene at Temperatures of (−15 to 80) °C[a]

t/°C	−15	0	20	25	30	40	50	60	70	80
$C^l(C_{60})$/g·dm^{-3}	5.90	5.55	4.02	4.00	4.18	4.82	4.18	3.95	3.83	n.d.
$C^l(C_{70})$/g·dm^{-3}	2.95	5.60	4.72	5.90	5.01	7.35	7.88	8.14	9.71	9.84
C^l(60 % wt C_{60} + 39 % wt C_{70} + 1 % wt C_{76}−C_{90})/g·dm^{-3}	n.d.	n.d.	9.4	11.0	11.0	13.6	11.6	9.3	6.8	n.d.

[a] $C^l(C_{60})$, concentration of C_{60} in solution; $C^l(C_{70})$, concentration of C_{70} in solution; C^l(60 % wt C_{60}+ 39 % wt C_{70}+ 1 % wt C_{76}−C_{90}), concentration of fullerene mixture in solution; n.d., not determined.

accuracy (Δ*D*) was equal to ± 0.005 (AU), and the absorption layer was 1 cm thick. The overall accuracy of determining concentrations of light fullerenes (C_{60} and C_{70}) in a saturated solution was no more than 5 %. Empirical formulas obtained for the fullerene solutions in aromatic solvents were as follows[16]

$$C(C_{60}) = 13.10(D_{335} - 1.808D_{472}) \quad (1)$$

$$C(C_{70}) = 42.51(D_{472} - 0.0081D_{335}) \quad (2)$$

where D_{335} and D_{472} are optical densities of the solutions referred to the absorption layer of 1 cm width and $C(C_{70})$ and $C(C_{60})$ represent the corresponding fullerene concentration (mg·dm^{-3}). The styrene solutions were preliminarily diluted with *o*-xylene, the reference solution being styrene solutions in *o*-xylene of the same dilution. Negligible admixtures of the heavy fullerenes $C_{N>70}$ were ignored.

Figure 1 shows visible and near UV absorption spectra of both fullerenes C_{60} and C_{70} and the standard fullerene mixture. As can be seen from Figure 1, the spectra are absolutely typical of the fullerene solutions in aromatic solvents,[18] which allowed us to use the empirical formulas 1 and 2. To check the results obtained, we used liquid chromatography (chromatograph Lumachrom from Lumex, St. Petersburg, Russia) with the absorption detection at 254 nm.[17] The results of both techniques used were in good agreement. The accuracy of determined fullerene concentrations in saturated solutions was ± (0.1 to 0.2) g·dm^{-3} depending on the fullerene concentration. The fullerene concentrations in solid solutions $(C_{60})_x(C_{70})_{1-x}$ and $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ were obtained in the same way after the dissolution of solid samples in excess *o*-xylene.

The following experimental method was used for the determination of the solvent content in solid crystal solutes. The solid phase deposited from styrene solution was filtered on a Schott filter (porosity factor 10), rinsed quickly with ethanol, and then dried for (10 to 15) min at 20 °C. Then, the solid phase was weighed, repeatedly washed with ethanol in a Soxhlete apparatus at 78 °C and 1 atm, dried for 1 h under vacuum (0.1 torr) at 200 °C, and weighed again. The weight change corresponded to the solvent content in the initial crystal solutes (or in the fullerene solid solution). The described experimental method for the determination of solid phase compositions was confirmed by the thermogravimetric analysis on Hungarian derivatograph Q-1500. The results of both methods are in a good agreement with each other.

Results and Discussion

The polythermal solubility of the C_{60} and C_{70} fullerenes and of the fullerene mixture (60 % wt of C_{60}, 39 % wt of C_{70}, 1 % wt of C_{76}−C_{90}) in styrene was measured with the aid of the isothermal saturation method at temperatures from (20 to 80) °C. In all cases, a multiple excess of fullerene as high as 400 mg of fullerene per 20 cm^3 of styrene was assured. Then, the solutions were saturated in a thermostatic shaker (temperature accuracy was within ± 0.1 °C) at the following temperatures: (20, 30, 40, 50, 60, 70, and 80) °C (for 8 h at each temperature). The duration of the experiment was predetermined by very long equilibration time in all investigated systems.

Table 2. Equilibrium Liquid−Solid Phase Composition in the Ternary System C_{60} + C_{70} + $C_6H_5CH{=}CH_2$ at Temperatures of (−15, 0, and 25) °C[a]

$C^l(C_{60})$ g·dm^{-3}	$C^l(C_{70})$ g·dm^{-3}	$W^l(C_{60})$ % wt	$W^s(C_{60})$ % wt	solid phase
		t = 25 °C		
4.02	0.00	1.00	1.00	$C_{60}\cdot 2C_6H_5CH{=}CH_2$
4.88	0.11	0.98	0.93	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
5.64	0.32	0.95	0.89	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
6.55	0.77	0.90	0.83	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
6.96	1.08	0.87	0.80	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.20	1.70	0.80	0.75	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.84	2.63	0.75	0.70	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
8.46	3.08	0.73	0.67	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
8.55	4.00	0.64	0.59	$(C_{60})_x(C_{70})_{1-x}$ + $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
6.03	3.99	0.60	0.50	$(C_{60})_x(C_{70})_{1-x}$
4.97	4.02	0.55	0.40	$(C_{60})_x(C_{70})_{1-x}$
2.61	4.30	0.39	0.30	$(C_{60})_x(C_{70})_{1-x}$
2.07	4.85	0.30	0.20	$(C_{60})_x(C_{70})_{1-x}$
1.27	5.25	0.19	0.15	$(C_{60})_x(C_{70})_{1-x}$
0.60	6.02	0.09	0.05	$(C_{60})_x(C_{70})_{1-x}$
0.00	6.02	0.00	0.00	$(C_{60})_x(C_{70})_{1-x}$
		t = 0 °C		
5.50	0.00	1.00	1.00	$C_{60}\cdot 2C_6H_5CH{=}CH_2$
6.84	1.29	0.84	0.89	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.22	2.17	0.77	0.86	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.24	2.39	0.76	0.81	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.69	3.57	0.76	0.74	$(C_{60})_x(C_{70})_{1-x}$ + $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
5.45	3.79	0.59	0.50	$(C_{60})_x(C_{70})_{1-x}$
4.99	4.20	0.54	0.38	$(C_{60})_x(C_{70})_{1-x}$
3.84	4.59	0.46	0.32	$(C_{60})_x(C_{70})_{1-x}$
2.53	5.38	0.32	0.23	$(C_{60})_x(C_{70})_{1-x}$
0	5.60	0.00	0.00	C_{70}
		t = −15 °C		
5.90	0.00	1.00	1.00	$C_{60}\cdot 2C_6H_5CH{=}CH_2$
6.41	0.49	0.93	0.86	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.16	1.23	0.85	0.84	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
7.84	2.62	0.75	0.71	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
8.01	3.56	0.69	0.66	$(C_{60})_x(C_{70})_{1-x}$ + $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$
5.33	2.69	0.66	0.46	$(C_{60})_x(C_{70})_{1-x}$
2.97	2.75	0.52	0.37	$(C_{60})_x(C_{70})_{1-x}$
2.01	2.78	0.42	0.26	$(C_{60})_x(C_{70})_{1-x}$
1.35	2.80	0.33	0.17	$(C_{60})_x(C_{70})_{1-x}$
0.31	2.82	0.1	0.09	$(C_{60})_x(C_{70})_{1-x}$
0.00	2.84	0.00	0.00	C_{70}

[a] $C^l(C_{60})$, concentration of C_{60} in solution; $C^l(C_{70})$, concentration of C_{70} in solution; $W^l(C_{60})$, mass fraction of the C_{60} fullerene in liquid solution; $W^s(C_{60})$, mass fraction of the C_{60} fullerene in solid solution.

The solubility in the ternary system C_{60} + C_{70} + $C_6H_5CH{=}CH_2$ at temperatures of (−15, 0, and 25) °C was investigated as follows. The mixtures with different weight proportions of unsolvated fullerenes and total weight of ∼ 400 mg were prepared. (The following proportions of C_{60}/C_{70} were considered: 1.00/0.00, 0.95/0.05, 0.90/0.10,..., 0.00/1.00.) Then, the mixtures were dissolved in excess *o*-xylene (∼ 100 cm^3) and filtered through the blue strip filter. Then, the solvent was entirely distilled off the samples in a vacuum oven at residual

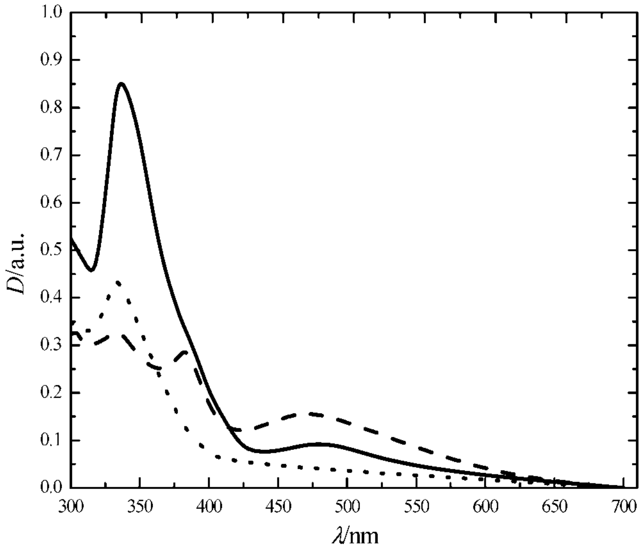

Figure 1. Optical spectra of the solutions of fullerenes: •••, C_{60}; ---, C_{70}; —, fullerene mixture. *D*, optical density; λ, wavelength. Fullerene concentrations ($g \cdot dm^{-3}$): C_{60}, 4.01; C_{70}, 4.72; fullerene mixture, 9.36.

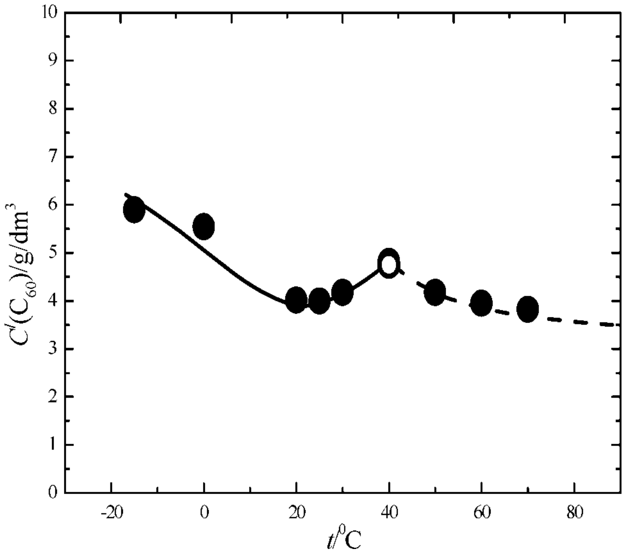

Figure 2. Polythermal solubility of C_{60} in styrene: —, crystallization of $C_{60} \cdot 2C_6H_5CH{=}CH_2$; ---, crystallization of C_{60}; ○, dissociation point of bisolvate ($C_{60} \cdot 2C_6H_5CH{=}CH_2 \rightarrow C_{60} + 2C_6H_5CH{=}CH_2$); $C^l(C_{60})$, concentration of C_{60} in solution.

pressure of < 0.1 torr. In this way, small ((1 to 10) μm) unsolvated particles of solid solutions $(C_{60})_x(C_{70})_{1-x}$ were formed. The heterogeneous mixtures were diluted with *o*-xylene (the fullerene was taken in apparent surplus (~ 400 mg of the fullerene per 20 cm^3 of styrene)) and then saturated at the selected temperatures ((−15 ± 0.5, 0 ± 0.2, and 25 ± 0.1) °C) in a thermostatic shaker. Saturation time was as long as 24 h because it was necessary to overcome the diffusion limitations. Such limitations always arise when solid solutions recrystallize because fullerene concentrations in liquid and solid solutions are different.

The phases of heterogeneous saturated solutions were separated on a Schott thermostatted filter (porosity factor 10).

Binary Systems

***$C_{60} + C_6H_5CH{=}CH_2$* System.** The polythermal solubility curve of the $C_{60} + C_6H_5CH{=}CH_2$ system is shown in Figure 2, whereas the corresponding data are represented in Table 1. The equilibrium phases were bisolvate $C_{60} \cdot 2C_6H_5CH{=}CH_2$ at low temperatures (≤ 40 °C) and unsolvated C_{60} at higher temperatures. The diagram is characterized by the only invariant point, ○, of so-called "pass-type". (According to ref 18, such points are characterized by combined saturation with both solid $C_{60} \cdot 2C_6H_5CH{=}CH_2$ and solid C_{60}.) It is just the point of the local solubility maximum. Similar maxima were observed earlier in systems with such aromatic solvents as toluene and *o*-xylene.[1−3,5−7,9]

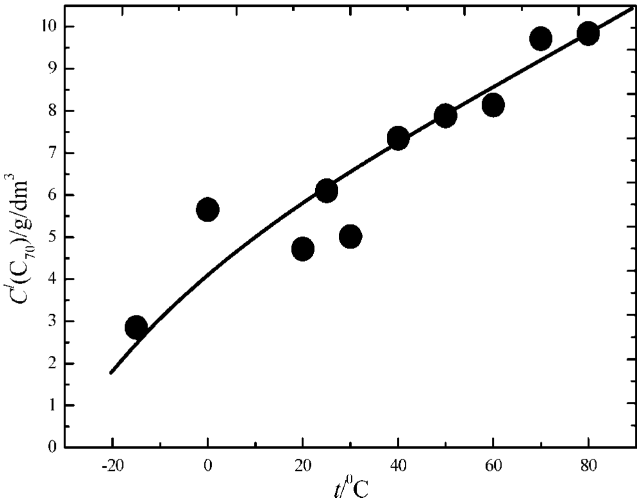

Figure 3. Polythermal solubility of C_{70} in styrene: —, crystallization of C_{70}; $C^l(C_{70})$, concentration of C_{70} in solution.

Unlike the high-temperature branch, the low-temperature branch of the bisolvate crystallizations reveals a minimum of solubility at 20 °C (Figure 2), which was not previously observed in similar systems. The presence of the minimum does not contradict the thermodynamics of heterogeneous systems.

To discuss this problem in more detail, we formulated the extended van der Waals differential equations for two-phase equilibrium.[19] The equilibrium liquid solution−solid bisolvate (l−s) was expressed via isobaric liquid phase quantities applied to the binary system fullerene C_{60}−styrene (f−x)

$$Q^{(l\rightarrow s)}/\{T(X_f^{(s)} - X_f^{(l)})[\partial^2 G^{(l)}/\partial X_f^{(l)2}]_{P,T}\} = dX_f^{(l)}/dT \qquad (3)$$

where $Q^{(l\rightarrow s)} = TS^{(l\rightarrow s)}$ is the heat effect of isothermal−isobaric phase crystallization, $X_f^{(s)}$and $X_f^{(l)}$ are molar fractions of the C_{60} fullerene in coexisting phases, $[\partial^2 G^{(l)}/\partial X_f^{(l)2}]_{P,T} > 0$ for a liquid solution stable against infinitesimal condition changes,[19] and $dX_f^{(l)}$ is a liquid solution quantity shift along the polythermal solution curve in binary system. Thus we can conclude that $dX_f^{(l)}/dT = 0$ if $Q^{(l\rightarrow s)} = 0$. Otherwise, the heat of crystallization of solid bisolvate from saturated liquid solution would change its sign. For example, solubility extremes in crystallization branches of the same solid phase in water + salt systems are common enough. They are typical of the systems with partially soluble salts. The handbook[20] quotes systems of salt−H_2O type, where salt is $UO_2F_2 \cdot 2H_2O$, $Ni(ClO_4)_2 \cdot 9H_2O$, $LiOH \cdot H_2O$, $REM_2(SeO_4)_3 \cdot xH_2O$ (where REM is La, Pr, Nd), or $LiB_5O_8 \cdot H_2O$. The authors of ref 20 did not analyze the data on the constant volume experiment or experiment on melting or segregation of the liquid phase. It is worth noticing that the solubility extrema were not observed in water-free salt crystallization branches[20] like in fullerenes systems.

***$C_{70} + C_6H_5CH{=}CH_2$* System.** The polythermal solubility curve of the $C_{70} + C_6H_5CH{=}CH_2$ system is shown in Figure 3, whereas the corresponding data are represented in Table 1. The only equilibrium solid phase in the C_{70}-containing system is

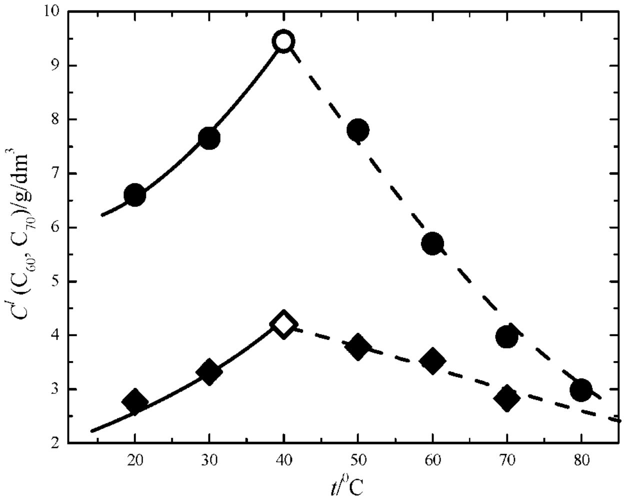

Figure 4. Polythermal solubility of C_{60} (●) and C_{70} (◆) fullerenes from their mixture. The fullerene solid solution composition was as follows: 60 % wt C_{60} + 39 % wt C_{70} + 1 % wt C_{76}−C_{90}. —, crystallization of $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$; ---, crystallization of $(C_{60})_x(C_{70})_{1-x}$; ○ and ◇, dissociation points of bisolvated solid solution $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2 \leftrightarrow (C_{60})_x(C_{70})_{1-x} + 2C_6H_5CH{=}CH_2$; $C^l(C_{60}, C_{70})$, concentrations of individual C_{60} or C_{70} in solution.

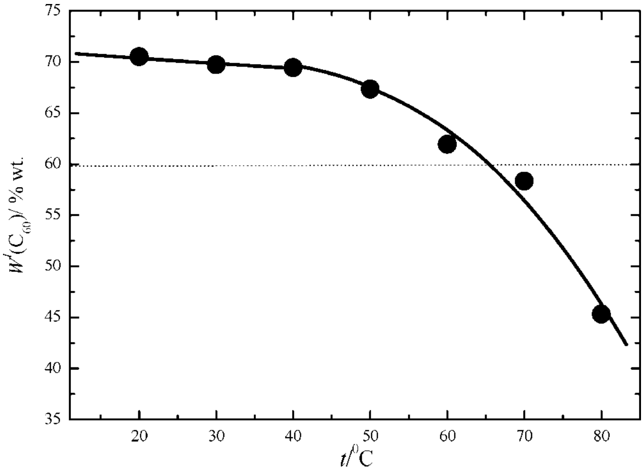

Figure 5. C_{60} fullerene content in saturated solution of the fullerene mixture against temperature: •••, initial starting solution (60 % wt C_{60} + 39 % wt C_{70} + 1 % wt C_{76}−C_{90}); $W^l(C_{60})$, mass fraction of the C_{60} fullerene in liquid solution.

unsolvated C_{70}. The solubility of the C_{70} fullerene monotonously increases with temperature like in the systems with different aromatic solvents such as toluene and *o*-xylene. (See, for example, refs 3 and 5.)

Fullerene Mixture (60 % C_{60} + 39 % C_{70} + 1 % C_{76-90}) + $C_6H_5CH{=}CH_2$. The polythermal solubility curve in the fullerene mixture + $C_6H_5CH{=}CH_2$ system is shown in Figure 4 (the corresponding data are in Table 1). The data on the solubility of the light fullerenes C_{60} and C_{70} from the mixture are shown separately for each fullerene in Figure 4.

Table 1 contains the total solubility of both fullerenes. In the last case, we assumed the presence of heavy fullerenes C_{76}−C_{90} to be negligible (1 % wt). Equilibrium solid phases in the system were the solid solutions bisolvate $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ at low temperature (≤ 40 °C) and the unsolvated solid solutions $(C_{60})_x(C_{70})_{1-x}$ at high temperatures. Each of two diagrams in Figure 4 has only one invariant "pass-type" point (○ in Figure 4) where the saturation of both solid solutions $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ and $(C_{60})_x(C_{70})_{1-x}$ occurs. Both fullerene components have their maximal solubility only in the point ○ (Figure 4). It should be noticed that the temperature of the desolvation reaction

$$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH = CH_2 \leftrightarrow (C_{60})_x(C_{70})_{1-x} + 2C_6H_5CH = CH_2 \quad (4)$$

for solid solutions of different composition (different *x*) is approximately constant [(∼ 40 ± 5) °C] and practically coincides with the temperature of the particular C_{60} desolvation process

$$C_{60}\cdot 2C_6H_5CH = CH_2 \leftrightarrow C_{60} + 2C_6H_5CH = CH_2 \quad (5)$$

This fact of coincidence is far from imperative from the viewpoint of thermodynamics, but we suppose that it is natural for solid solution enriched with fullerene C_{60}.

Ternary C_{60} + C_{70} + $C_6H_5CH{=}CH_2$ System. The diagrams of the solubility and fullerene component distribution between liquid and solid solutions in the ternary system C_{60} + C_{70} + $C_6H_5CH{=}CH_2$ at temperatures (−15, 0, and 25) °C are shown in Figures 6, 7, 8, and 9. As can be seen from Figures 6, 7, and 8, the solubility diagrams consist of two branches. One branch

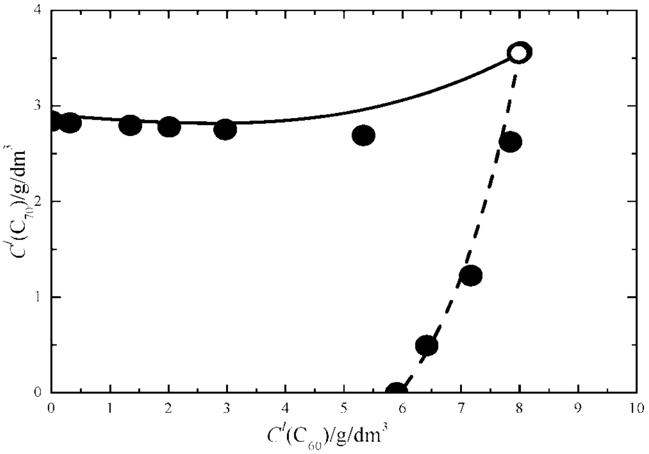

Figure 6. Solubility diagram in the ternary system C_{60} − C_{70} − $C_6H_5CH{=}CH_2$ at temperature −15 °C. —, crystallization of $(C_{60})_x(C_{70})_{1-x}$; ---, crystallization of $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$; $C^l(C_{60})$, concentration of C_{60} in solution; $C^l(C_{70})$, concentration of C_{70} in solution; ○, simultaneous saturation of two solids.

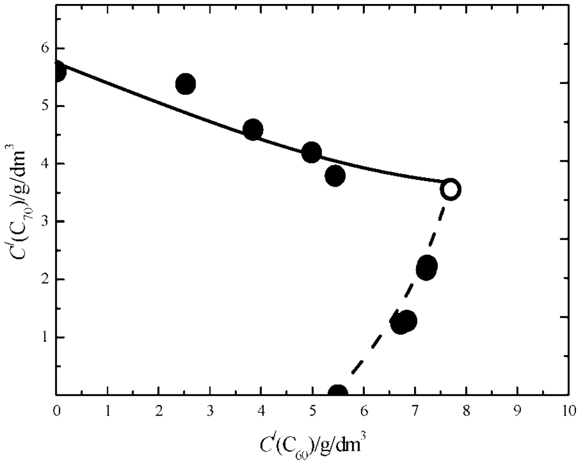

Figure 7. Solubility diagram in the ternary system C_{60} − C_{70} − $C_6H_5CH{=}CH_2$ at temperature 0 °C. —, crystallization of $(C_{60})_x(C_{70})_{1-x}$, ---, crystallization of $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$; $C^l(C_{60})$, concentration of C_{60} in solution; $C^l(C_{70})$, concentration of C_{70} in solution; ○, simultaneous saturation of two solids.

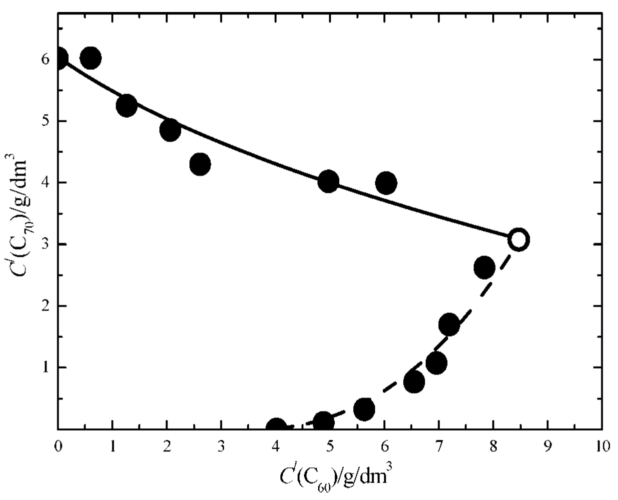

Figure 8. Solubility diagram in the ternary system $C_{60}-C_{70}-C_6H_5CH{=}CH_2$ at temperature 25 °C. —, crystallization of $(C_{60})_x(C_{70})_{1-x}$; ---, crystallization of $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$; $C^l(C_{60})$, concentration of C_{60} in solution; $C^l(C_{70})$, concentration of C_{70} in solution; ○, simultaneous saturation of two solids.

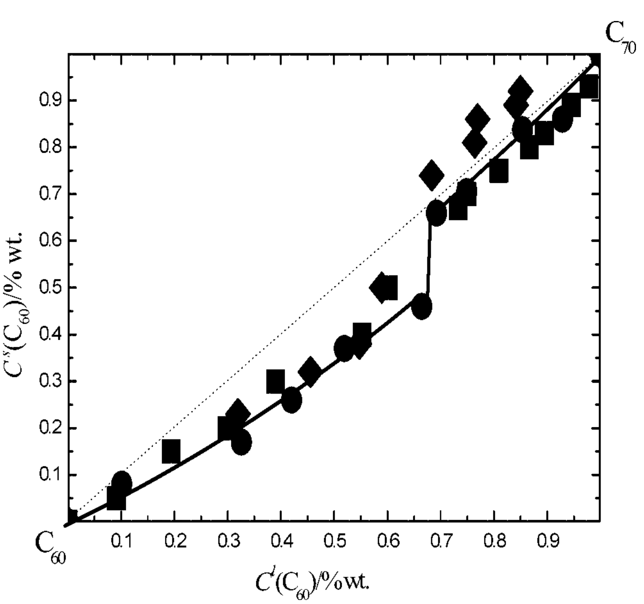

Figure 9. Fullerene component distribution between liquid and solid solutions in the ternary system $C_{60} + C_{70} + C_6H_5CH{=}CH_2$. ■, 25 °C; ♦, 0 °C; ●, −15 °C; $C^l(C_{60})$, mass fraction of the C_{60} fullerene in liquid solution; $C^s(C_{60})$, mass fraction of the C_{60} fullerene in solid solution.

corresponds to the crystallization of the bisolvated solid solutions $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ enriched with the C_{60} fullerene. The other branch corresponds to the crystallization of unsolvated solid solutions $(C_{60})_x(C_{70})_{1-x}$ enriched with the fullerene C_{70}. At any temperature, there is the only invariant point (○ in Figures 6, 7, and 8) that corresponds to the simultaneous saturation of two solids. (See ref 18.) The fullerene distribution diagrams contain miscibility gap regions for solid-phase compositions when the mass ratio C_{60}/C_{70} is in the range of 0.53 to 1 (Figure 9). The bisolvated solid solutions enriched with the C_{60} fullerene reveal the salting-in effect in the branches of crystallization; that is, in the saturated solutions, the concentration of C_{60} fullerene increases with the concentration of the C_{70} fullerene (Figures 6, 7, and 8). On the contrary, in the branches of crystallization of unsolvated solid solutions enriched with the C_{70} fullerene, the salting-out effect is observed at temperatures of (0 and 25) °C; that is, in the saturated solutions, the concentration of the C_{70} fullerene monotonously decreases with the increase in the C_{60} fullerene concentration (Figures 7 and 8). The salting-in effect for the C_{60} fullerene is observed again in the crystallization branch of unsolvated solid solutions enriched with the C_{70} fullerene at −15 °C (Figure 6).

Conclusions

We have investigated the solubility in the ternary system $C_{60} + C_{70} + C_6H_5CH{=}CH_2$ and its binary subsystems over a wide temperature range. Equilibrium solid phases in the C_{60}-containing systems at low (≤ 40 °C) and high temperatures are bisolvate $C_{60}\cdot 2C_6H_5CH{=}CH_2$ and unsolvated C_{60}, respectively. The only equilibrium solid phase in the C_{70}-containing system is unsolvated C_{70}. The solubility of the C_{70} fullerene monotonously increases with temperature, whereas the temperature dependence of the C_{60} fullerene solubility has both a minimum and a maximum. The solubility diagrams of the ternary system $C_{60} + C_{70} + C_6H_5CH{=}CH_2$ at temperatures (−15, 0, and 25) °C are shown to consist of two branches. The first branch corresponds to the crystallization of bisolvated solid solutions $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ enriched with the fullerene C_{60}, whereas the second branch corresponds to the crystallization of unsolvated solid solutions $(C_{60})_x(C_{70})_{1-x}$ enriched with the fullerene C_{70}. At any temperature, there is only one invariant point that corresponds to simultaneous saturation with the two solid solutions. During crystallization, the immixing regions for solid-state components are observed if the mass ratio $C_{60}/(C_{60} + C_{70})$ is within the range from 0.35 to 0.50. The salting-in effect is observed in the crystallization branches of the bisolvated solid solutions enriched with the C_{60} fullerene; that is, the concentration of C_{60} increases with the concentration of C_{70} in saturated solutions. On the contrary, in the crystallization branches of unsolvated solid solutions enriched with the C_{70} fullerene, the salting-out effect is observed; that is, the concentration of the C_{70} fullerene monotonously decreases with the increase in the C_{60} fullerene concentration.

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