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Temperature Dependence of Solubility of Individual Light Fullerenes and Industrial Fullerene Mixture in 1-Chloronaphthalene and 1-Bromonaphthalene

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The paper presents some data on the temperature dependence of solubility of individual light fullerenes (C_{60} and C_{70}) and industrial fullerene mixtures ($w_1 = 0.65\ C_{60} + w_2 = 0.34\ C_{70} + w_3 = 0.01\ C_n$ ($n = 76$ to 90)) in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C. Solubility and density temperature dependences are presented and characterized; compositions of equilibrium solid phases are determined.

Introduction

Information on light fullerene solubility is important for example in the development of the chromatographic and prechromatographic methods of light fullerene separation, in the development of medical and cosmetic products, in the elaboration of fullerene extraction and separation from industrial fullerene soot, and in the study of chemical reactions involving fullerenes.[1−3]

An analysis of the literature data on light fullerene solubility in various solvents reveals the following trends in the investigation of solid−liquid equilibrium with the participation of fullerenes:

(1) The binary systems consisting of an individual light fullerene (C_{60} or C_{70}) and a solvent are the most investigated, and in this context various classes of organic and inorganic solvents have been studied (alkanes, alkenes, carboxylic acids, alcohols, aromatic solvents, etc.).[2−11] It is significant that most of the data are devoted to the investigation of fullerene isothermal solubility (mainly at (20 to 25) °C); for example, the isothermal solubility of the C_{60} fullerene is investigated in 180 solvents, and the isothermal solubility of the C_{70} fullerene is investigated in more than 40 solvents. Because of the inaccessibility of the C_{70} fullerene, the data on solubility in the C_{70}−solvent binary systems are limited.

An analysis of the literature data on the isothermal solubility of the individual light fullerenes (C_{60}, C_{70}) at room temperature reveals the following regularities:[2,3]

(i) Solubilities of C_{60} and C_{70} are of one order but can differ several times; namely, the difference in solubilities can underlie the most efficient method of fullerene separation.

(ii) Fullerenes are practically insoluble in polar solvents and poorly soluble in acyclic saturated hydrocarbons (they are more soluble, with the greater number of carbon atoms in a solvent molecule); this indicates the insufficient role of the solvation mechanism of dissolution.

(iii) The maximum solubility of fullerene is observed in solvents whose specific enthalpy of dissolution related to the volume of the solvent molecule is close to the corresponding value of the fullerene molecule. Aromatic hydrocarbons and their derivatives can be examples of such solvents. They represent the most effective solvents for the elaboration of chromatographic and prechromatographic methods of separation of light fullerenes. By now the solubility of the C_{60} fullerene has been investigated in the following aromatic solvents: benzene,[1,12,13] toluene,[1,12,13,15−20] 1,2-dimethylbenzene,[12,18,19,21,22] 1,3-dimethylbenzene,[12] 1,4-dimethylbenzene,[12] 1,2,3-trimethylbenzene,[23] 1,2,4-trimethylbenzene,[23] 1,3,5-trimethylbenzene,[1,16,12] 1,2,3,4-tetramethylbenzene,[23] 1,2,3,5-tetramethylbenzene,[12] tetralin,[1,13,24,25] ethylbenzene,[12] *n*-propylbenzene,[12] isopropylbenzene,[12] *n*-butylbenzene,[12] *sec*-butylbenzene,[12] fluorobenzene,[1,12] chlorobenzene,[1,12] bromobenzene,[1,12] iodobenzene,[12] 1,2-dichlorobenzene,[1,12,24−28] 1,2-dibromobenzene,[12,29] 1,3-dichlorobenzene,[12,26] 1,3-dibromobenzene,[12,29] 1,2,4-trichlorobenzene,[1,12,14,27,29] styrene,[30,31] *o*-cresol,[1] benzonitrile,[1] nitrobenzene,[1] 1,3-diphenylacetone,[25] anisole,[13] *p*-bromoanisole,[13] *m*-bromoanisole,[2] benzaldehyde,[2] phenyl isocyanate,[2] thiophenol,[2] 1-methyl 2-nitrobenzene,[2] 1-methyl-3-nitrobenzene,[2] benzyl chloride,[2] benzyl bromide,[2] 1,1,1-trichloromethylbenzene,[1] 1-methylnaphthalene,[1,12,32] 1-phenylnaphthalene,[1] 1-chloronaphthalene,[1,32] 1-bromo-2-methylnaphthalene,[12] 1,2-dimethylnaphthalene,[13] and thiophenol.[13]

In the case of the C_{70} fullerene the isothermal solubility was investigated in narrower number of solvents, namely, in the following: benzene,[33] 1,4-dimethylbenzene,[33] 1,3,5-trimethylbenzene,[29,34] 1,3-dichlorobenzene,[35] mesitylen,[33] styrene,[30,31] 1,2-dichlorobenzene,[24,33] 1,2-dimethylbenzene,[18,22] toluene,[15,18,33] tetralin,[34] and 1,3-diphenylacetone.[2]

As can be found in relevant literature, the polythermal solubility of individual C_{60} has been investigated in 30 solvents, while the polythermal solubility of C_{70} has been studied in more than 20 solvents. In the case of aromatic solvents, the polythermal solubility of the C_{60} fullerene was studied in benzene,[27] 1,2-dimethylbenzene,[18] toluene,[18,36,39] 1,2-dichlorobenzene,[24,27,28] 1,2,4-trichlorobenzene,[27] 1,3-diphenylacetone,[24] tetraline,[24] and styrene[30,31] and for the C_{70} fullerene in toluene,[18] 1,2-dimethylbenzene,[18] 1,2-dichlorobenzene,[24] tetralin,[24] 1,3-diphenylacetone,[24] and styrene.[30,31]

For the systems chosen in the context of this research the only data presented in literature are the data on isothermal solubility (at 20 °C) in the binary system C_{60}−1-chloronaph-

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thalene. The solubility values are equal to (51.00, 51.68,[32] and 51.28) g·L^{-1}.[47]

By now the polybaric solubility of fullerenes was investigated only for two binary systems, namely, C_{60} + hexane[38] and C_{60} + toluene.[37] Sawamura and Fujita have for the first time investigated polythermo-polybaric solubility of individual C_{60} fullerene in toluene in a wide range of temperatures and pressures.[37]

(2) The data on the solubility of light fullerenes in ternary systems are scarce in spite of the fact that these data are important in developing chromatographic and prechromatographic methods of separation. The solubility in two ternary systems [C_{60} + C_{70} + *o*-xylene at (253, 298, and 353) K and C_{60} + C_{70} + styrene at (258, 273, and 293) K] has been studied by our group,[30,31,22] while Korobov et al. studied the first system at 298 K.[19] In the case of another type of ternary systems (C_{60} + C_{70} + solvent), the data on solubility are presented in literature only for several systems: decaline + naphthalene, toluene + naphthalene, dodecane + naphthalene, acetonitrile + toluene, toluene + acetonitrile, toluene + ethanol, toluene + tetrahydrofuran, acetonitrile + tetrahydrofuran, ethanol + water, tetrahydrofuran + water, tetrachloromethane + toluene, and tetrachloromethane + *o*-diclorobenzene.[3,28,40,43,48]

(3) The data on the solubility of the light fullerenes in multicomponent systems (natural oils, animal fats, essential oils) are extremely important due to the following reasons:[41−46,48]

(i) Fullerenes are rather soluble in natural solvents in the mentioned temperature range. The solubility varies from a tenth of the unit grams of fullerene per liter of solvent.

(ii) Fullerene solutions in natural solvents represent stable and absolutely transparent true solutions. These solutions are absolutely nontoxic and biocompatible with respect to animals and humans.

(iii) Fullerene solutions in oils and fats possess pronounced antibacterial and antioxidative properties; they can absorb free radicals and ion radicals from condensed phases in which they are present as well as photons in the ultraviolet area of the spectrum.

In the work presented here, the binary systems of individual light fullerene + chloro(bromo)naphthalene as well as pseudobinary systems of the industrial fullerene mixture ($w_1 = 0.65$ C_{60} + $w_2 = 0.34$ C_{70} + $w_3 = 0.01$ C_n (n = 76 to 90)) + chloro(bromo)naphthalene were chosen for the following reasons:

(i) As can be seen from literature, the solubility of light fullerenes in aromatic solvents is quite high (for the C_{60} fullerene, from 1.5 g·L^{-1} in benzene up to 27 g·L^{-1} in 1,2-dichlorobenzene; for the C_{70} fullerene, from 1.3 g·L^{-1} in benzene up to 36 g·L^{-1} in 1,2-dichlorobenzene).[2] However, solubility values of fullerenes in naphthalenes are noticeably higher: (51.00,[1] 51.68,[32] and 51.28[47]) g·L^{-1} in 1-chloronaphthalene, (33.00,[1] 34.78,[32] 33.20,[12] and 35.64[47]) g·L^{-1} in 1-methylnaphthalene, 50.00 g·L^{-1} in phenylnaphthalene,[1] 34.78 g·L^{-1} in 1-bromo-2-methylnaphthalene,[32] and 36.00 g·L^{-1} in 1,2-dimethylnaphthalene.[13]

(ii) It is possible to carry out the (inter)polymerization of fullerenes in solution for obtaining surfaces of a new type.

(iii) Owing to high fullerene solubility in 1-halogen naphthalenes this kind of research is important for the realization of the high-performance extraction process of the fullerene mixture from the fullerene soot.

(iv) There is an opportunity for effective extraction of residual fullerene mixture from different sorbents for the chromatographic separation of fullerenes (for example, carbon norrit, azo, or carbonized silochroms or carbonized silica).[49]

Materials and Methods

We used fullerenes C_{60} of 99.9 % purity and C_{70} of 99.5 % purity (from ILIP Ltd., St. Petersburg) with controllable principal admixtures of C_{70} in C_{60} and C_{60} in C_{70} of 0.1 and 0.5 %, correspondingly. The composition of standard fullerene mixture (from ILIP Ltd., St. Petersburg) was $w_1 = 0.65$ C_{60} + $w_2 = 0.34$ C_{70} + $w_3 = 0.01$ C_n (n = 76 to 90). The other reagents used were reagent grade *o*-xylene, 1-chloronaphthalene, and 1-bromonaphthalene (from Vecton Ltd., St. Petersburg).

An experimental investigation of the individual light fullerene and industrial fullerene mixture ($w_1 = 0.65$ C_{60} + ww C_n (n = 76 to 90)) solubility in various solvents in the temperature range from (10 to 60) °C was carried out by the isothermal saturation method. First of all solutions of C_{60}, C_{70}, and fullerene mixture in 1-chloronaphthalene and 1-bromonaphthalene were prepared (in all cases the excess amount of solid phase was used). Then the solutions were stirred in a temperature-controlled shaker at a particular fixed temperature for a period not shorter than 20 h. The long duration of the experiment is connected with the long duration of the equilibrium state reaching that in the concerned systems.

The concentrations of fullerenes C_{60} and C_{70} in liquid styrene were measured using the spectrophotometric technique (on double-beam spectrophotometer "SPECORD M40" made in Germany, Karl Zeiss) at characteristic wavelengths of (335 and 472) nm corresponding to maximum absorbance. The wavelengths do not change with changing of solvent. The accuracy of wavelength maintenance is ± 0.5 nm, and the photometric accuracy (ΔD) is equal to ± 0.005 (a.u.) with the 1 cm thick absorption layer. The overall relative uncertainty of determining the composition of light fullerenes (C_{60} and C_{70}) in saturated solution does not exceed 5 %.

Calculations of the light fullerene (C_{60}, C_{70}) concentrations in liquid solutions were realized on the basis of empirical equations obtained for fullerene solutions in aromatic solvents by the spectrophotometric method:[50−53]

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

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

where D_{335} and D_{472} represent the optical densities of solutions referred to the absorbance layer thickness equal to 1 cm; $C(\mathrm{C_{60}})$ and $C(\mathrm{C_{70}})$ represent the concentrations of the fullerenes in saturated solutions (mg·L^{-1}). The halogen naphthalene solutions were preliminarily diluted with *o*-xylene, the reference solutions being 1-chloro(bromo)naphthalene solutions in *o*-xylene at the same dilution. Negligible admixtures of the high fullerenes $C_{N>70}$ were ignored.

In the electronic absorption spectra of solutions of individual fullerenes and industrial fullerene mixtures ($w_1 = 0.65$ C_{60} + $w_2 = 0.34$ C_{70} + $w_3 = 0.01$ C_n (n = 76 to 90)) in 1-chloronaphthalene and 1-bromonaphthalene, solvatochromic effects (sharp change of the optical spectrum at moderate change of the solution concentration or solvent composition) characteristic for two-component mixtures (acetonitrile + toluene, benzene + methanol, benzene + hexane, etc.) and suggesting tendency toward the formation of fullerene clusters do not appear.[51−53] Thus, fullerene solutions in 1-chloronaphthalene and 1-bromonaphthalene are similar to solutions in aromatic solvents (*o*-xylene, benzene, toluene, *o*-dichlorobenzene). This justifies the use of empirical eqs 1 and 2 in this case.[50]

For the examination of spectrophotometric data we used the liquid chromatography technique (liquid chromatograph, Lumachrom, St. Petersburg, Russia), the light-absorbance being detected at 254 nm. Results obtained by two independent methods are in good agreement with each other. The accuracy of measuring of light fullerene concentrations in saturated solutions was about ± (0.1 to 0.2) $g \cdot L^{-1}$ depending on the current fullerene concentration.[54]

The experimental method for the determination of the solvent content in solid crystal solutes was as follows. The heterogeneous mixtures consisting of the solvent (1-chloronaphthalene or 1-bromonaphthalene) and corresponding solid phases (individual C_{60}, individual C_{70}, fullerene mixture) in 10-fold excess (in comparison with solubility value) were prepared. After that the mixtures were saturated at 20 °C during 72 h. Then the liquid phase was separated from the solid phase by filtrating on a fine filter; the isolated solid phases were analyzed using the experimental gravimetric and derivatographic method. In the first method the solid phase deposited from 1-chloro(bromo)naphthalene solutions was rinsed fast by ethanol after filtration and then dried at 20 °C during (10 to 15) min. Then the solid phase was weighed, repeatedly washed with ethanol in the Soxhlete apparatus at 78 °C and 1 atm, dried in vacuum (13.3 Pa) at 200 °C for 1 h, and weighed again. The composition of solid solvates of individual fullerenes (C_{60}, C_{70}) or solvated solid solutions was determined from the solid-phase mass change. The described experimental method for the determination of solid-phase composition was confirmed by the thermogravimetric analysis on Hungarian derivatograph Q-1500 (MOM, Hungary). The results of both methods are in good agreement. An analysis of the experimental data on the composition of solid solvates reveals that in all binary and pseudobinary systems the solid phase represents sesquisolvated individual light fullerenes and sesquisolvated solid solutions. The experimental results on the composition of solid solvates are in keeping with the literature data.[47]

The density temperature dependences for solutions saturated by individual light fullerenes (C_{60}, C_{70}) as well as by industrial fullerene mixture in 1-halogen naphthalenes are presented in Table 1. The data were obtained by weighting aliquots of saturated solutions of fullerenes at controlled temperature. The volume of the aliquots was 100 ± 1 μL. Several factors influence the density temperature dependence: the density values of 1-chloronaphthalene and 1-bromonaphthalene decrease with increasing temperature, densities of the dissolved individual light fullerenes as well as the density of the industrial fullerene mixture decrease with increasing temperature, and finally, the nonmonotonic temperature dependence of density can be caused by a change of the type of a light fullerene solid solvate which is in equilibrium with the saturated solution. However, in our case, this effect was not observed.

Table 1. Temperature Dependence of the Solubility of Individual Light Fullerenes (C_{60} and C_{70}) and Industrial Fullerene Mixtures ($w_1 = 0.65\ C_{60} + w_2 = 0.34\ C_{70} + w_3 = 0.01\ C_n$ (n = 76 to 90)) in 1-Chloronaphthalene and 1-Bromonaphthalene in the Temperature Range from (20 to 60) °C[a]

solvent	ρ / $g \cdot cm^{-3}$	C / $g \cdot L^{-1}$	100 w	ρ / $g \cdot cm^{-3}$	C / $g \cdot L^{-1}$	100 w
t/°C		10			20	
Solubility of the C_{60} Fullerene						
1-chloronaphthalene	1.32	26	2.0	1.27	20	1.6
1-bromonaphthalene	1.53	28	1.8	1.51	25	1.7
Solubility of the C_{70} Fullerene						
1-chloronaphthalene	1.37	275	20	1.34	263	20
1-bromonaphthalene	1.61	295	18	1.58	279	18
Solubility of the Industrial Fullerene Mixture[b]						
1-chloronaphthalene	1.33	61	4.6	1.29	104	8.1
		31	2.3		34	2.7
1-bromonaphthalene	1.55	87	5.6	1.55	110	7.1
		50	3.2		52	3.4
t/°C		30			40	
Solubility of the C_{60} Fullerene						
1-chloronaphthalene	1.21	19	1.5	1.17	20	1.7
1-bromonaphthalene	1.49	27	1.8	1.45	30	2.1
Solubility of the C_{70} Fullerene						
1-chloronaphthalene	1.27	345	27	1.25	402	34
1-bromonaphthalene	1.55	299	19	1.53	346	23
Solubility of the Industrial Fullerene Mixture[b]						
1-chloronaphthalene	1.23	120	9.8	1.21	117	9.7
		30	2.4		40	3.3
1-bromonaphthalene	1.54	121	7.9	1.50	117	7.8
		51	3.3		48	3.2
t/°C		50			60	
Solubility of the C_{60} Fullerene						
1-chloronaphthalene	1.17	24	2.1	1.16	35	3.0
1-bromonaphthalene	1.46	36	2.5	1.47	41	2.8
Solubility of the C_{70} Fullerene						
1-chloronaphthalene	1.21	542	37	1.30	695	54
1-bromonaphthalene	1.52	380	25	1.51	389	26
Solubility of the Industrial Fullerene Mixture[b]						
1-chloronaphthalene	1.21	105	8.7	1.22	99	8.1
		36	3.0		39	3.2
1-bromonaphthalene	1.49	107	7.2	1.48	95	6.5
		54	3.6		68	4.6

[a] The data presented for 60 °C are evaluative. ρ is the density of solution ($g \cdot cm^{-3}$); C is the volume concentration of the corresponding fullerene ($g \cdot L^{-1}$); w_{C_n} is the bulk mass concentration of the corresponding fullerenes. [b] The upper value corresponds to the solubility of C_{60} from the fullerene mixture; the lower value corresponds to the solubility of C_{70} from fullerene mixture.

Results and Discussion

The data on the solubility of the individual light fullerenes, C_{60} and C_{70}, as well as the data on the solubility of the main components of the industrial fullerene mixture in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C are presented in Table 1 and Figures 1 to 3, correspondingly.

The temperature dependences of solubility presented in Figures 1 to 3 are the fragments of the low-temperature branches of the solubility polytherms; at the end of these branches (in the invariant point)[55] the incongruent melting process of the fullerene solvates takes place.

Thus, the solid phase equilibrated with the saturated solution in the case of binary systems of individual light fullerene (C_{60} or C_{70}) + 1-chloro(bromo)naphthalene is the sesquisolvated individual fullerene. In the case of pseudobinary system of industrial fullerene mixture + 1-chloro(bromo)naphthalene the solid phase equilibrated with the saturated solution over the temperature range from (10 to 60) °C is the sesquisolvated solid solution.

An analysis of the temperature dependences of solubility of light fullerenes in 1-chloronaphthalene and 1-bromonaphthalene reveals the following regularities:

(i) In the case of binary systems of C_{60} + 1-chloronaphthalene and C_{60} + 1-bromonaphthalene the increase in solubility values with increasing temperature takes place; however, the low-temperature branch of the sesquisolvate crystallizations in the C_{60} + 1-chloronaphthalene system reveals a minimum of solubility at 30 °C (Figure 1). This fact was observed previously in the low-temperature branch of crystallization of the bisolvated C_{60} fullerene in the binary system C_{60} + styrene.[31] The presence of the minimum does not contradict the thermodynamics of

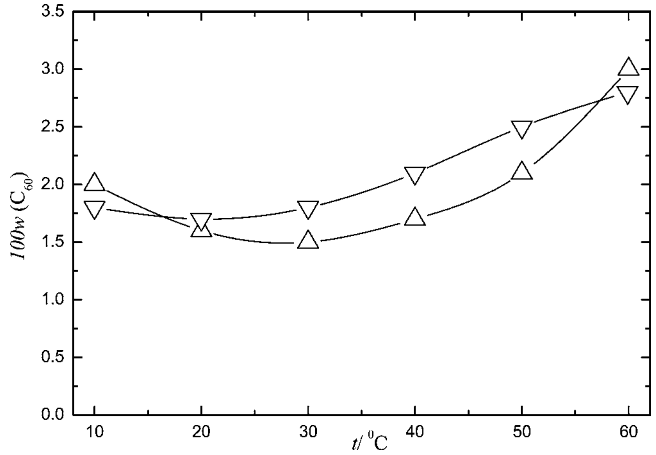

Figure 1. Mass fraction solubility *w* of the C_{60} fullerene in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C. △, solubility of the C_{60} fullerene in 1-chloronaphthalene; ▽, solubility of the C_{60} fullerene in 1-bromonaphthalene.

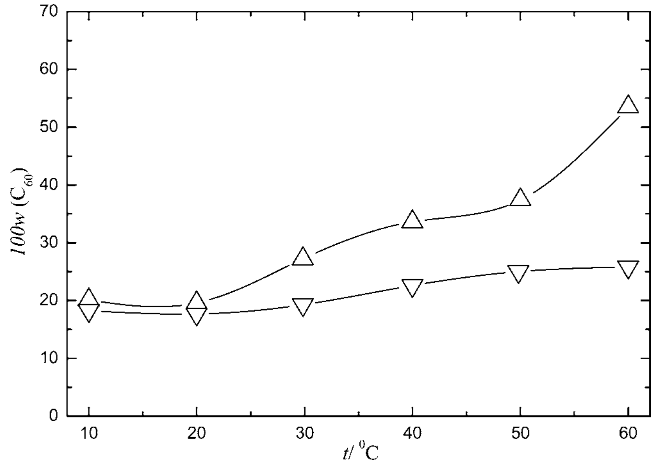

Figure 2. Mass fraction solubility *w* of the C_{70} fullerene in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C. △, solubility of the C_{70} fullerene in 1-chloronaphthalene; ▽, solubility of the C_{70} fullerene in 1-bromonaphthalene.

heterogeneous systems. To discuss this problem in more detail, the extended van der Waals differential equations for two-phase equilibrium[56] were formulated. The equilibrium liquid solution (l)−solid bisolvate (s) were expressed via isobaric liquid phase quantities, applied to the binary system: fullerene C_{60} (f)-styrene (x):

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

where $Q^{(l\to s)} = TS^{(l\to s)}$ is the heat effect of isothermal−isobaric phase crystallization, $X_f^{(s)}$ and $X_f^{(l)}$ are molar fractions of the fullerene C_{60} in coexisting phases, $[\partial^2 G^{(l)}/\partial X_f^{(l)2}]_{P,T} > 0$ for a liquid solution, stable against infinitesimal condition changes,[56] and $dX_f^{(l)}$ is a liquid solution quantity shift along the polythermal solution curve in the binary system. This way, we can conclude that $dX_f^{(l)}/dT = 0$ if $Q^{(l\to s)} = 0$. Otherwise, the heat of crystallization of solid sesquisolvate from saturated liquid solution changes its sign. For example, solubility extremes in crystallization branches of the same solid phase in water−salt systems are met often enough. They are typical to the systems with partially soluble salts. The handbook[57] quotes systems of salt + H_2O type, where salt = $UO_2F_2\cdot 2H_2O$, $Ni(ClO_4)_2\cdot 9H_2O$, $LiOH\cdot H_2O$, $REM_2(SeO_4)_3\cdot xH_2O$ (REM = La, Pr, Nd), and $LiB_5O_8\cdot H_2O$.

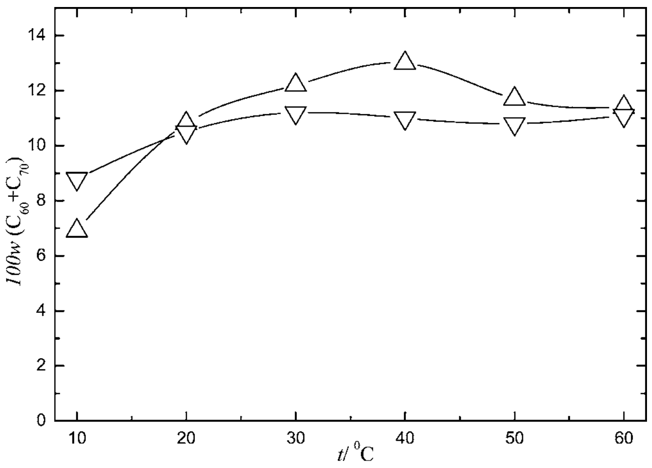

Figure 3. Total solubility of the components (C_{60}, C_{70}) of the industrial fullerene mixtures ($w_1 = 0.65$ C_{60} + $w_2 = 0.34$ C_{70} + $w_3 = 0.01$ C_n (n = 76 to 90)) in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C. △, solubility of the (C_{60} + C_{70}) mixture in 1-chloronaphthalene; ▽, solubility of the (C_{60} + C_{70}) mixture in 1-bromonaphthalene.

(ii) An analysis of the polythermal solubility of the industrial fullerene mixture components shows that the difference in solubility values of the main components (C_{60} and C_{70}) is from 2 to 6 times; this fact allows us to propose the investigated systems for the prechromatographic separation of fullerene mixtures.

(iii) A comparison of the solubility temperature dependences in the case of binary systems (individual light fullerene + solvent) shows that the solubility of the C_{70} fullerene is several times higher than solubility of the C_{60} fullerene (Figure 2). The phenomenon of higher solubility of C_{70} is determined by the higher polarizabillity of this fullerene ($8\cdot 10^{-23}$ cm^3) in comparison with C_{60} ($6.4\cdot 10^{-23}$ cm^3).[58] In the case of fullerene mixture (Figure 3) the opposite effect was observed: the solubility value of the C_{60} fullerene from the fullerene mixture exceeds the solubility of C_{70} (see Table 1).

Conclusions

The authors have investigated solubility in binary and pseudobinary systems consisting of individual light fullerenes (C_{60}, C_{70}) and industrial fullerene mixtures ($w_1 = 0.65$ C_{60} + $w_2 = 0.34$ C_{70} + $w_3 = 0.01$ C_n (n = 76 to 90)) in 1-chloronaphthalene and 1-bromonaphthalene. Temperature dependences of solubility and density are presented and characterized, and the relevance of this kind of research is discussed. We have established that light fullerenes and solid solutions based on them form the solid crystal solvates which contain one and a half molecules of the corresponding solvent.

Supporting Information Available:

Optical spectra of fullerene solutions in 1-chloronaphthalene and 1-bromonaphthalene; the photos of solid solvates $C_{70}\cdot 1.5C_{10}H_7Cl$ and $C_{70}\cdot 1.5C_{10}H_7Br$ made on a polarizing microscope; temperature dependences of density of the C_{60} fullerene, C_{70} fullerene, and industrial fullerene mixture solutions in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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