Solubility of Light Fullerenes in Organic Solvents

Konstantin N. Semenov,*,† Nikolai A. Charykov,‡ Viktor A. Keskinov,‡ Andrey K. Piartman,‡ Alexander A. Blokhin,‡ and Aleksei A. Kopyrin§

Saint-Petersburg State University, St. Petersburg, Russia, 198504, Universitetskii pr. 26, ILIP Ltd. (Innovations of Leningrad Universities and Enterprises), St. Petersburg, Russia, 197022, Instrumentalnaya ul. 6, and Saint-Petersburg State Technological Institute (Technological University), St. Petersburg, Russia, 190013, Moskovskii pr. 26

Experimental and literature data concerning the solubility of individual light fullerenes (C_{60} and C_{70}) in binary (individual fullerene + solvent), ternary (C_{60} + C_{70} fullerenes + solvent; C_{60} or C_{70} fullerenes + solvent 1 + solvent 2), and multicomponent (fullerenes + natural fats and oils) systems as well as the data on solubility of industrial fullerene mixtures and fullerene derivatives in various organic solvents are presented and discussed.

Introduction

A knowledge of the light fullerenes solubility is important in, for example, the development of the chromatographic and prechromatographic methods for the separation of light fullerenes, in the development of medical and cosmetic products, in the elaboration of the extraction and separation of fullerenes from industrial fullerene soot, and in the study of chemical reactions involving fullerenes.

The solubility of light fullerenes in a range of solvents has been reported in the literature. Nevertheless, an analysis of the literature data reveals lack of some data and sometimes ambiguities in the available experimental data. Characteristic features of the available data are the following:

The lack of data on the solubility of light C_{70} fullerene in binary systems in comparison with the C_{60} fullerene. For example, at 298 K (sometimes at 293 K), the solubility of the C_{60} has been measured in approximately 150 solvents, whereas the solubility of the C_{70} has been measured only in 70 solvents (see Tables 1 and 2). The solubility data (at 293 K) of individual light fullerenes (C_{60}, C_{70}) in homological series of 1-alcohols and 1-alkanoic acids are presented in Figures 1 to 4 as an example.

Solubility of individual light fullerenes over a temperature range has been investigated for a still narrower number of solvents. Thus, in the case of the C_{60} fullerene, solubility has been measured in solvents such as hexane,[40] heptane,[6] tetralin,[21] carbon disulfide,[40] *n*-butylamine,[24] benzene,[24] toluene,[18,40] *o*-xylene,[18] *o*-dichlorobenzene,[21,24,42] 1,2,4-trichlorobenzene,[24] 1,3-diphenylacetone,[21] thiophene,[24] tetrahydrothiophene,[24] tetrahydrofurane,[24] 1-alkanoic acids with normal structure,[57−59] 1-alkanols,[13] styrene,[25] carbon disulfide,[4,18,40] and natural fats and oils.[29,30] Solubility of the C_{70} fullerene as a function of temperature has been investigated in the following solvents: heptane,[6] tetralin,[21] toluene,[17,18,46] *o*-xylene,[18] *o*-dichlorobenzene,[21] 1,3-diphenylacetone,[21,37] 1-alkanoic acids,[51] 1-alkanols,[52] carbon disulfide,[18] styrene,[25] and natural fats and oils.[29,30]

Data on the solubility of fullerene mixtures in a single solvent are limited. The solubility in the ternary systems C_{60} + C_{70} + *o*-xylene at (253, 298, and 353) K[9] and C_{60} + C_{70} + styrene at (258, 273, and 293) K has been studied by our group,[9] while Korobov studied the first system at 298 K.[16] Moreover, we have measured the solubility of the fullerene mixture (60 % C_{60} + 39 % C_{70} + 1 % $C_{76\div90}$) in the homologous series of 1-alkanoic acids, 1-alkanols, natural fats and oils, styrene, and heptane.

The solubilities for systems consisting of individual fullerene and mixed solvent are extremely scarce. Only a few studies have been published. The temperature dependences of the light fullerene solubility in high isomeric carboxylic acids, natural oils, animal fats, and essential oils have been studied in our group.[10]

Experimental Section

In the present work, the solubility of light fullerenes in binary systems (individual light fullerenes (C_{60}, C_{70}) + oleic, linolic, and octadecatrienoic acids), pseudobinary systems (industrial fullerene mixture + oleic, linolic, and linolenic acids), and ternary systems (C_{60} + C_{70} + $C_6H_4Cl_2$ at 423 K) was investigated.

The C_{60} fullerene of mass fraction w = 99.9 % and the C_{70} fullerene of w = 99.5 % (purchased from ILIP Ltd., St.-Petersburg) with controlled principal admixtures C_{70} in C_{60} and C_{60} in C_{70} of mass fraction (0.1 and 0.5) %, respectively, were used. The mass fraction of a standard fullerene mixture (purchased from ILIP Ltd., St.-Petersburg) was 60 % of C_{60} + 39 % of C_{70} + 1 % of C_{76}−C_{90}. The other reagents used were reagent-grade *o*-xylene, 1,2-dichlorobenzene, oleic, linolic, and linolenic acids.

The concentrations of C_{60} and C_{70} fullerenes in the liquid phase were measured with the aid of a spectrophotometric technique (using the double-beam spectrophotometer "SPECORD M40", Karl Zeiss, Germany) at wavelengths of (335 and 472) nm corresponding to the maximum absorbances which are stable relative to a solvent change. The uncertainty of the wavelength was ± 0.5 nm; photometric uncertainty ΔD (l = 1 cm) was equal to ± 0.005 units of optical density; and the absorption layer was 1 cm thick. The overall uncertainty of determining concentrations of light fullerenes (C_{60} and C_{70}) in a saturated

* Corresponding author. Tel.: (812)3476435. Fax: (812)2349859. E-mail: semenov1986@yandex.ru.
† Saint-Petersburg State University.
‡ ILIP Ltd.
§ Saint-Petersburg State Technological Institute.

10.1021/je900296s CCC: $40.75
Published on Web 09/30/2009

Table 1. Solubility (S) of C_{60} in Various Solvents at 298 K (Temperatures Different from 298 K Are Presented in Brackets)[a]

solvent	S/g·L^{-1}	ref	solvent	S/g·L^{-1}	ref
		Alkanes			
pentane (C_5H_{12})	***0.005***	1	isooctane (C_8H_{18})	0.026	2
	0.004 (303 K)	2		0.028	4
	0.003	3		***0.027***	
	0.007	4	nonane (C_9H_{20})	0.062	3
hexane (C_6H_{14})	0.043	1		0.034	4
	0.040	2		***0.048***	
	0.037	3	decane ($C_{10}H_{22}$)	0.071	1
	0.052	5		0.070 (303 K)	2
	0.046	4		***0.072***	4
2-methylpentane (C_6H_{14})	0.019	3	dodecane ($C_{12}H_{26}$)	0.091	2
3-methylpentane (C_6H_{14})	0.025	3		0.103	4
	0.048	3		***0.097***	
heptane (C_7H_{16})	0.027	6		0.126	2
	0.302	7	tetradecane ($C_{14}H_{28}$)	0.168	4
	0.025 (303 K)	2		***0.147***	
octane (C_8H_{18})	***0.020***	3			
	0.302	7			
	0.025	4			
		Cyclic Alkanes			
cyclopentane (C_5H_{10})	0.002	1	methylcyclohexane (C_7H_{14})	0.17	10
	0.036	1	1,2-dimethylcyclohexane, mixture of cis and trans (C_8H_{16})	0.13	10
	0.051 (303 K)	2	ethylcyclohexane (C_8H_{16})	0.25	10
cyclohexane (C_6H_{12})	0.036	8	3:7 mixture of *cis*- and *trans*-decalins ($C_{10}H_{18}$)	4.60	1
	0.036	5		***1.87***	11
	0.035	9	*cis*-decalin($C_{10}H_{18}$)	2.20	1
	0.054	4	*trans*-decalin ($C_{10}H_{18}$)	1.30	1
cyclohexene (C_6H_{10})	1.21	10	1,5,9-cyclododecatriene ($C_{12}H_{18}$)	7.14	10
1-methyl-1-cyclohexene ($C_6H_9CH_3$)	1.03	10			
		Haloalkanes			
dichloromethane (CH_2Cl_2)	0.26	1	1,1,1-trichloroethane (Cl_3CCH_3)	0.15	8
	0.25 (303 K)	2	1-chloropropane (C_3H_7Cl)	0.02	10
	0.23	8	2-chloropropane ($(CH_3)_2CHCl$)	0.01	7
	0.25		1-bromopropane (C_3H_7Br)	0.05	8
trichloromethane ($CHCl_3$)	0.16	1	2-bromopropane (C_3H_7Br)	0.03	7
	0.17	10	1-iodopropane (C_3H_7I)	0.17	8
	0.51	4	2-iodopropane (C_3H_7I)	0.11	8
	0.28		1,2-dichloropropane ($C_3H_6Cl_2$)	0.10	8
tetrachloromethane (CCl_4)	0.32	1	1,3-dichloropropane ($C_3H_6Cl_2$)	0.12	8
	0.45 (303 K)	2	(±)-1,2-dibromopropane ($C_3H_6Br_2$)	0.35	8
	0.10	12	1,3-dibromopropane ($C_3H_6Br_2$)	0.40	10
	0.27	43	1,3-diiodopropane ($C_3H_6I_2$)	2.77	8
dibromomethane (CH_2Br_2)	0.36	8	1,2,3-trichloropropane ($C_3H_5Cl_3$)	0.64	8
tribromomethane ($CHBr_3$)	5.64	8	1,2,3-tribromopropane ($C_3H_5Br_3$)	8.31	8
iodomethane (CH_3I)	0.77	8	1-chloro-2-methylpropane (C_4H_9Cl)	0.03	8
diiodomethane (CH_2I_2)	0.13	8	1-bromo-2-methylpropane (C_4H_9Br)	0.089	10
bromochloromethane (CH_2BrCl)	0.75	10	1-iodo-2-methylpropane (C_4H_9I)	0.34	8
bromoethane (C_2H_5Br)	0.07	10	2-chloro-2-methylpropane ($(CH_3)_3CCl$)	0.01	10
iodoethane (C_2H_5I)	0.28	10	2-bromo-2-methylpropane ($(CH_3)_3CBr$)	0.06	10
trichloroethylene (C_2HCl_3)	1.40	1	2-iodo-2-methylpropane ($(CH_3)_3CI$)	0.230	10
tetrachloroethylene (C_2Cl_4)	1.20	1	bromobutane (C_4H_9Br)	1.20	7
dichlorodifluoroethane ($C_2H_2Cl_2F_2$)	0.02	1	cyclopentyl bromide (C_5H_9Br)	0.41	8
1,1,2-trichlorotrifluoroethane ($ClCF_2CCl_2F$)	0.01	1	cyclohexyl chloride ($C_6H_{11}Cl$)	0.53	8
1,1,2-trichloroethane ($ClCH_2CHCl_2$)	0.130	1	cyclohexyl bromide ($C_6H_{11}Br$)	2.20	8
1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$)	5.30	1	cyclohexyl iodide ($C_6H_{11}I$)	8.06	8
1,2-dibromoethylene (BrCH=CHBr)	1.84	8	(±)-*trans*-1,2-dibromocyclohexane ($C_6H_{10}Br_2$)	14.3	7
1-chloro-2-methylpropene ($(CH_3)_2C=CHCl$)	0.21	7	bromoheptane ($C_7H_{15}Br$)	2.297	7
1,2-dichloroethane ($C_2H_4Cl_2$)	0.08	8	bromooctane ($C_8H_{17}Br$)	3.398	7
	0.50	1	1-bromotetradecane ($CH_3(CH_2)_{13}Br$)	6.19	7
1,2-dibromoethane ($C_2H_4Br_2$)	0.54	8	1-bromooctadecane ($CH_3(CH_2)_{17}Br$)	6.19	7
	0.52				
		Natural Oils			
≪Stavropolje≫ (unrefined sunflower oil)	0.451 (293 K)	29	linseed oil	0.513 (293 K)	29
≪Zlato≫ (refined sunflower oil)	0.377 (293 K)	29		0.365	32
sunflower triglyceride	0.116	33		53.1[b] (328 K)	47
sunflower oil ≪Venus≫	6.91	31	linseed triglyceride	0.091	33
sunflower oil ≪Floriol≫	4.01	31	pignolia oil	0.485 (293 K)	29
sunflower oil ≪Eden≫	5.62	31	grape-seed oil	0.371 (293 K)	29
≪Milora≫ (corn oil)	0.609 (293 K)	29	apricot-kernel oil	0.509 (293 K)	29
walnut oil	0.485 (293 K)	29	brassica methyl ester (biodiesel)	0.187	33
	0.470 (293 K)	29	soybean triglyceride	0.859	32
olive oil	0.00461 (303 K)	31	castor oil	0.392	32
	0.909	32	peanut oil	0.751	32
	23.6[b] (323 K)	47	sunseed oil	0.522	32
olive oil ≪Carapelli≫	2.84	31	soybean oil	0.495	32
olive oil ≪Borgess≫	5.97	31	sea-buckthorn oil	43.2[b] (328 K)	47
olive oil ≪Olatalia≫	3.97	31	cedur oil	51.8[b] (343)	47
olive triglyceride	0.173	33	mixture of cedur oil and sea-buckthorn oil	47.5[b] (333 K)	47

Table 1. Continued

solvent	S/g·L^{-1}	ref	solvent	S/g·L^{-1}	ref
			Animal Fats		
pork fat	0.052 (323 K)	34	lamb fat	0.041 (323 K)	34
bird fat	0.024 (323 K)	34	desi	0.021 (323 K)	34
beef fat	0.041 (323 K)	34	molten cow butter	soluble	32
margarine ≪Rumjashka≫	0,019 (323 K)	34	cod-liver oil	53.0[b] (328 K)	47
			Essential Oils		
essential oil of carnation	1.551 (293 K)	35	essential oil of cypress	20.6[b] (323 K)	47
essential oil of lemon	18.8[b] (323 K)	47	essential oil of eucalyptus	23.4[b] (323 K)	47
essential oil of orange	21.3[b] (329 K)	47	gum spirit	25.6[b] (338 K)	47
			Inorganic Solvents		
water (H_2O)	$1.3 \cdot 10^{-11}$	3	hexachlorodisilane ($(SiCl_3)_2$)	0.38	41
silicon(IV) chloride ($SiCl_4$)	0.09	41	silicon(IV) bromide ($SiBr_4$)	0.74 (305 K)	41
germanium(IV) chloride ($GeCl_4$)	0.50	41	germanium(IV) bromide ($GeBr_4$)	0.68 (305 K)	41
tin(IV) chloride ($SnCl_4$)	1.23	41	tin(IV) bromide ($SnBr_4$)	0.17 (305 K)	41
			Alcohols		
	0.000035	3	heptan-1-ol ($C_7H_{15}OH$)	0.0694	13
methanol (CH_3OH)	***0.000024***	13		0.0468	3
	0.000027	14		0.152	13
	0.001	1	octan-1-ol ($C_8H_{17}OH$))	0.0429	14
	0.0014	97		***0.0389***	14
ethanol (C_2H_5OH)	***0.0012***	13		0.0429	97
	0.0014	14	distilled octanol	0.0389	97
	0.0008	3	nonan-1-ol ($C_9H_{19}OH$)	0.214	13
	0.0041	3	decan-1-ol ($C_{10}H_{21}OH$)	0.270	13
propan-1-ol (C_3H_7OH)	0.0083	13	undecan-1-ol ($C_{11}H_{23}OH$)	0.354	13
	0.0062		propan-2-ol (C_3H_7OH)	0.0021	3
	0.0094	3	butan-2-ol (C_4H_9OH)	0.0036	3
butan-1-ol (C_4H_9OH)	***0.0345***	13	pentan-2-ol ($C_5H_{11}OH$)	0.0180	3
	0.030	3	pentan-3-ol ($C_5H_{11}OH$)	0.0288	3
pentan-1-ol ($C_5H_{11}OH$)	***0.0388***	13	propan-1,3-diol ($C_3H_8O_2$)	0.0009	3
	0.042	3	butan-1,4-diol ($C_4H_{10}O_2$)	0.0022	3
hexan-1-ol ($C_6H_{13}OH$)	***0.0640***	13	pentan-1,5-diol ($C_5H_{12}O_2$)	0.0044	3
			Carboxylic Acids		
acetic acid ($C_2H_4O_2$)	0.0068	16	octanoic acid ($C_8H_{16}O_2$)	0.0473	16
propionic acid ($C_3H_6O_2$)	0.0156	16	nonanoic acid ($C_9H_{18}O_2$)	0.161	16
butanoic acid ($C_4H_8O_2$)	0.0141	16	linolic acid ($C_{18}H_{32}O_2$)	34.2[b] (323)	47
pentanoic acid ($C_5H_{10}O_2$)	0.058	16	oleic acid ($C_{18}H_{34}O_2$)	22.4[b] (313 K)	47
hexanoic acid ($C_6H_{12}O_2$)	0.184	16	octadecatrienoic acid ($C_{18}H_{30}O_2$)	35.5[b] (325 K)	47
heptanoic acid ($C_7H_{14}O_2$)	0.279	16			
			Aromatic Hydrocarbons		
	1.70	1		7.00	1
	1.50	15	chlorobenzene (C_6H_5Cl)	5.70	15
benzene (C_6H_6)	1.44 (303 K)	16		***6.35***	
	0.88	7		3.30	1
	1.40	4	bromobenzene (C_6H_5Br)	2.80	15
	2.80	1		***3.05***	
	2.90	15	iodobenzene (C_6H_5I)	2.10	15
	2.29	17		27.00	1
	2.15 (303 K)	2		24.60	15
	2.27	5		***22.90***	21
	2.90	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	7.11	24
toluene (C_7H_8)	***2.40***	7		22.9	22
	3.20	4		23.40	23
	3.00	14		27.04	42
	2.9	19	1,2-dibromobenzene ($C_6H_4Br_2$)	13.80	15, 44
	0.54	8		2.40	15
	2.44	41	1,3-dichlorobenzene ($C_6H_4Cl_2$)	5.03	23
	8.70	15		***3.72***	
	7.35	8	1,3-dibromobenzene ($C_6H_5Br_2$)	13.80	15, 44
	9.30	18		8.50	1
1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	9.5	19		10.40	15
	7.7	20	1,2,4-trichlorobenzene ($C_6H_3Cl_3$)	4.85	24
	9.25	50		21.31	4
	1.40	15		***9.62***	44
1,3-dimethylbenzene ($C_6H_4(CH_3)_2$)	2.83	8	styrene ($C_6H_5CH{=}CH_2$)	3.75	10
	2.11			4.00	25, 28
	5.90	15		***3.88***	
1,4-dimethylbenzene ($C_6H_4(CH_3)_2$)	3.14	8	*o*-cresol ($CH_3C_6H_4OH$)	0.01	1
	4.52		benzonitrile (C_6H_5CN)	0.41	1
1,2,3-trimethylbenzene ($C_6H_3(CH_3)_3$)	4.70	11	nitrobenzene ($C_6H_5NO_2$)	0.80	1
1,2,4-trimethylbenzene ($C_6H_3(CH_3)_3$)	17.90	11	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	1.45	22
	1.50	1	anisole ($CH_3OC_6H_5$)	5.60	7
	1.00 (303 K)	2	*p*-bromoanisole ($CH_3OC_6H_4Br$)	16.78	7
1,3,5-trimethylbenzene ($C_6H_3(CH_3)_3$)	1.70	15	*m*-bromoanisole ($CH_3OC_6H_4Br$)	16.20	8
	1.60		benzaldehyde (C_6H_5CHO)	0.42	8
1,2,3,4-tetramethylbenzene ($C_6H_2(CH_3)_4$)	5.80	11	phenyl isocyanate (C_6H_5NCO)	2.44	10
1,2,3,5-tetramethylbenzene ($C_6H_2(CH_3)_4$)	20.80	15	thiopheno l(C_6H_5SH)	6.91	8
	16.00	1	1-methyl 2-nitrobenzene($C_6H_7NO_2$)	2.43	8
	14.62	21	1-methyl 3-nitrobenzene ($C_6H_7NO_2$)	2.36	8
tetralin ($C_{10}H_{12}$)	15.70	7	benzyl chloride ($C_6H_5CH_2Cl$)	2.40	8
	14.5 (295)	22	benzyl bromide ($C_6H_5CH_2Br$)	4.94	8
	2.60	15	1,1,1-trichloromethylbenzene ($C_7H_5Cl_3$)	4.80	1
ethylbenzene ($C_6H_5C_2H_5$)					

Table 1. Continued

solvent	S/g·L^{-1}	ref	solvent	S/g·L^{-1}	ref
	2.16	8		33.00	1
	2.38		1-methylnaphthalene ($C_{10}H_7CH_3$)	34.78	45
n-propylbenzene ($C_6H_5C_3H_7$)	1.50			15	***33.20***	15
isopropylbenzene ($C_6H_5CH(CH_3)_2$)	1.20	15	1-phenylnaphthalene ($C_{10}H_7C_6H_5$)	50.00	1
n-butylbenzene ($C_6H_5C_4H_9$)	1.90	15		51.00	[1]
sec-butylbenzene ($C_6H_5CH(CH_3)CH_2CH_3$)	1.10	15	1-chloronaphthalene ($C_{10}H_7Cl$)	51.68	45
	0.59	1		***51.34***	
fluorobenzene (C_6H_5F)	1.20	15	1-bromo,2-methylnaphthalene ($CH_3C_{10}H_6Br$)	34.78	15
	0.90		1,2-dimethylnaphthalene ($C_{10}H_6(CH_3)_2$)	36.00	7
			thiophenol (C_6H_5SH)	6.91	7
		Other Polar Solvents			
nitromethane (CH_3NO_2)	***0.000***	1	acrylonitrile (CH_2═$CHCN$)	0.0040	10
	0.216	7	*n*-butylamine ($CH_3(CH_2)_3NH_2$)	3.688	39
nitroethane ($C_2H_5NO_2$)	0.002	1	2-methoxyethyl ether ($(CH_3OCH_2CH_2)_2O$)	0.032	8
acetone (CH_3COCH_3)	0.001	1	*N*,*N*-dimethylformamide ($HCON(CH_3)_2$)	0.027	8
acetonitrile (CH_3CN)	0.000	1	1,4-dioxane ($C_4H_8O_2$)	0.041 (303 K)	2
	0.0004	14			
		Miscellaneous			
	7.90	1	2-methylthiophene (C_5H_6S)	6.80	1
	5.16 (303 K)	2	pyrrolidine (C_4H_9N)	47.52	7
carbon disulfide (CS_2)	7.70	18	*N*-methyl-2-pyrrolidone (C_5H_9NO)	0.89	1
	7.49	40		0.89	1
	11.81	4	pyridine (C_5H_5N)	0.30	15
	7.90	41		**0.60**	
	0.40	15	piperidine ($C_5H_{11}N$)	53.28	7
thiophene (C_4H_4S)	0.24	24	2,4,6-trimethylpyridine ($C_8H_{11}N$)	8.71	7
	0.32		tetrahydrothiophene (C_4H_8S)	0.03	1
	0.06	1	quinoline (C_9H_7N)	7.20	15
	0.58	7			
tetrahydrofuran (C_4H_8O)	0.04	4			
	0.011	14, 97			

[a] We have marked out by black and italic type the solubility values that are the most probable *in our opinion*. In the cases when the only value is presented, this value is the most probable. [b] Saturation of fullerene solutions was carried out using ultrasonic machining.

solution is no more than 5 %. Empirical formulas, obtained for the fullerene solutions, were as follows[6,13,27,29,30]

$$C(C_{60})/mg{\cdot}L^{-1} = 13.10(D_{335} - 1.808D_{472}) \quad (1)$$

$$C(C_{70})/mg{\cdot}L^{-1} = 42.51(D_{472} - 0.0081D_{335}) \quad (2)$$

where D_{335} and D_{472} are optical densities of the solutions with regard to the absorption layer of 1 cm width and $C(C_{70})$ and $C(C_{60})$ are the fullerene concentrations.

All solutions were preliminarily diluted with *o*-xylene, the reference solution being *o*-dichlorobenzene, oleic, linolic, and linolenic acids in *o*-xylene with the same dilution.

To check the results, liquid chromatography (chromatograph Lumachrom from Lumex Ltd., St.-Petersburg, Russia) with absorption detection at 254 nm was used The results of both techniques were in a good agreement (relative difference ± 3 %). The uncertainty of determined fullerene concentrations in saturated solutions was ± (0.1 to 0.2) g·L^{-1} depending on the fullerene concentration. The fullerene concentrations in solid solutions were obtained in the same way after dissolution of solid samples in excess of *o*-xylene.

The following experimental method was used for determination of the solvent content in solid crystal solutes. The solid phase deposited from solution was filtered with a Schott filter (porosity factor 10), rinsed quickly with ethanol, and then dried for (10 to 15) min at 293 K. Then, the solid phase was weighted, repeatedly washed with ethanol in a Soxhlete apparatus at 351 K and 1 atm, dried for 1 h in vacuum (13.3 Pa) at 473 K, and weighted again. The mass change corresponded to the solvent content in the initial crystal solutes (or in the fullerene solid solution). The method for determination of the solid phase compositions was confirmed by the thermogravimetric analysis on a Hungarian derivatograph Q-1500. The results of both methods are in good agreement with each other (relative difference ± 10 %).

In Table 3 and Figure 5 the temperature dependences of solubility of the individual light fullerenes (C_{60} and C_{70}) in oleic, linolic and linolenic acids are presented, in one's turn the polytherms of solubility of the components of the industrial fullerene mixture (C_{60} and C_{70}) are presented in Table 4 and Figure 6 correspondingly. Such kind of investigation can be extremely actual due to the following reasons:

From the general considerations, the light fullerenes solubility in such acids should be higher than in the corresponding saturated analogues (the light fullerene solubility varies from 1/10 to 1/100 mg·L^{-1}). On the other hand, these acids are important components of fats, and they are biologically compatible with mammalians.

The other possible way of application of the light fullerene compositions with unsaturated fatty acids is the elaboration of the tribological additives to fuel and technical oils. It is significant that the compositions with unsaturated fatty acids mainly based on oleic acid (due to its cheapness) are with much success used for this purpose. Tables 3 and 4 and Figures 5 and 6 show the following:

−the solubility values in all studied unsaturated fatty carboxylic acids vary from 1/10 g·L^{-1} up to 10 g·L^{-1}. It is worthwhile to say that these values are 1 to 2 orders higher than in the case of earlier studied saturated carboxylic acids;

−the solubility values of the both light fullerenes in all studied unsaturated carboxylic acids increase with increasing temperature (in the case of individual light fullerenes (C_{60}, C_{70}) and components of industrial fullerene mixture): $dS_{acid}(C_{60})/dT > 0$ and $dS_{acid}(C_{70})/dT > 0$;

−in all cases, the individual solubility of the more polarizable fullerene C_{70} is higher than the solubility value of ≪pseudo-

Table 2. Solubility of C_{70} in Various Solvents at 298 K (Temperatures Different from 298 K Are in Brackets)[a]

solvent	S/g·L^{-1}	ref	solvent	S/g·L^{-1}	ref
			Alkanes		
n-pentane (C_5H_{12})	0.002	46	*n*-octane (C_8H_{18})	0.042	46
n-hexane (C_6H_{14})	0.013	46	*n*-decane ($C_{10}H_{22}$)	0.053	46
	0.047	46	dodecane ($C_{12}H_{26}$)	0.098	46
n-heptane (C_7H_{16})	0.031	6	cyclohexane (C_6H_{12})	0.08	46
	0.039				
			Alcohols		
methan-1-ol (CH_3OH)	***0.0004***	52	hexan-1-ol ($C_6H_{13}OH$)	***0.126***	52
	0.00004	49		0.035	49
ethan-1-ol (C_2H_5OH)	***0.0007***	52	heptan-1-ol ($C_7H_{15}OH$)	0.046	52
	0.00078	49	octan-1-ol ($C_8H_{17}OH$)	***0.027***	52
propan-1-ol (C_3H_7OH)	***0.003***	52		0.046	49
	0.0039	49	nonan-1-ol ($C_9H_{19}OH$)	0.190	52
isopropanol ($(CH_3)_2CHOH$)	0.0021	46	decan-1-ol ($C_{10}H_{21}OH$)	0.310	52
butan-1-ol (C_4H_9OH)	***0.013***	52	undecan-1-ol ($C_{11}H_{23}OH$)	0.229	52
	0.0086	49	molten behenamide ($CH_3(CH_2)_{20}CONH_2$)	soluble	32
pentan-1-ol ($C_5H_{11}OH$)	***0.021***	52			
	0.00028	49			
			Natural Oils		
≪Stavropolje≫ (unrefined sunflower oil)	1.827	30	pignolia oil	0.757	29
≪Zlato≫ (refined sunflower oil)	1.289	30	apricot-kernel oil	1.009	29
≪Milora≫ (corn oil)	1.957	30	castor oil	0.636	32
walnut oil	1.390	30	peanut oil	0.852	32
olive oil	0.756	30	sunseed oil	0.867	32
	1.035	32	soybean oil	0.753	32
linseed oil	1.198	30	brassica oil	1.034	32
	0.727	32			
			Aromatic Solvents		
benzene (C_6H_6)	1.3	46		15.6	18
p-xylene ($C_6H_4(CH_3)_2$)	3.99	46	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	15.17	50
	1.47	53		15.4	
1,3,5-trimethylbenzene ($C_6H_3(CH_3)_3$)	1.45	44		1.5	18
	1.46		toluene ($C_6H_5CH_3$)	1.406	46
1,3-dichlorobenzene ($C_6H_4Cl_2$)	18.7	48		1.07	17
mesitylen ($C_6H_3(CH_3)_3$)	1.472	46	tetralin ($C_{10}H_{12}$)	12.3	53
styrene ($C_6H_5CH{=}CH_2$)	4.72	27	1,3-diphenylacetone ($C_6H_5CH_2)_2CO$)	1.45 (297.1 K)	37
	36.21	46			
1,2-dichlorobenzene ($C_6H_4Cl_2$)	22.9	21			
	29.6				
			Carboxylic Acids		
formic acid (CH_2O_2)	0.0002	51	hexanoic acid ($C_6H_{12}O_2$)	0.125	51
acetic acid ($C_2H_4O_2$)	0.0005	51	heptanoic acid($C_7H_{14}O_2$)	0.330	51
propanoic acid ($C_3H_6O_2$)	0.002	51	octanoic acid ($C_8H_{16}O_2$)	0.110	51
butanoic acid ($C_4H_8O_2$)	0.013	51	nonanoic acid ($C_9H_{18}O_2$)	0.056	51
pentanoic acid ($C_5H_{10}O_2$)	0.014	51	molten stearic acid ($CH_3(CH_2)_{16}COOH$)	soluble	32
			Animal Fats		
pork fat (323 K)	0.143	34	margarine ≪Rumjashka≫ (323 K)	0.080	34
bird fat (323 K)	0.148	34	lamb fat (323 K)	0.053	34
beef fat (323 K)	0.054	34	desi (323 K)	0.159	34
			Other Solvents		
acetone (CH_3COCH_3)	0.0019	46		15.3	18
dichloromethane (CH_2Cl_2)	0.08	46	carbon disulfide (CS_2)	9.875	46
tetrachloromethane (CCl_4)	0.121	46		10.16	17
water (H_2O)	$1.1^{*}\cdot10^{-13}$	49			

[a] We have marked out by black and italic type the solubility values that are the most probable in our opinion. In the cases when the only value is presented, this value is the most probable.

spheroid≫ C_{60}. This fact is quite typical for the solvents with the high solubility values of the light fullerenes;

−the solubility value of the C_{60} from the industrial fullerene mixture is higher than the solubility value of individual C_{60}; the ≪salting-in≫ effect of the C_{60} fullerene takes place in the branch of crystallization of the solid solutions enriched by C_{60};

−with the increase of the unsaturation degree of the carboxylic acid, the solubility values of both light fullerenes increase: the solubility of fullerenes in trienoic acid is higher than in dienic acid, and solubility values in dienic acid are higher than in ≪monoenic≫ acid;

−we can consider that both of the light fullerenes in the solid phase are unsolvated.

The diagram of solubility along with the diagram of fullerene components distribution between liquid and solid solutions in the ternary system $C_{60} + C_{70} + C_6H_4Cl_2$ at 423 K are shown in Figures 7 and 8 and Table 5.

As can be seen from Figure 7, the solubility diagram consists of two branches. One corresponds to crystallization of the unsolvated solid solutions $(C_{60})_x(C_{70})_{1-x}$ enriched with the C_{60} fullerene. The other corresponds to 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 ("E" in Figure 7) corresponding to simultaneous saturation of two solids. 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 0.25 to 0.7 (Figure 8). The unsolvated solid solutions enriched with the C_{60} and C_{70} fullerenes reveal the salting-in effect in the branches of crystallization; i.e., in the saturated solutions, the concentration of the C_{60} fullerene increases with the concentration of the C_{70} fullerene, and the

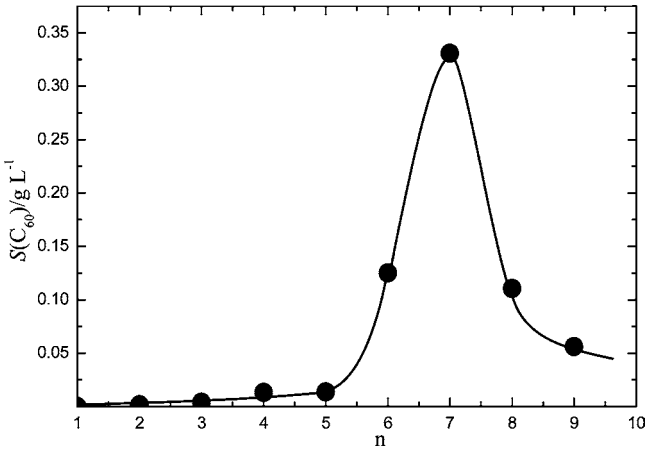

Figure 1. Solubility of the C_{60} fullerene in the homological series of 1-alkanoic carboxylic acid $C_nH_{2n+1}COOH$ (*n*, number of the carbon atoms in the hydrocarbon chain) at $T = 293$ K.

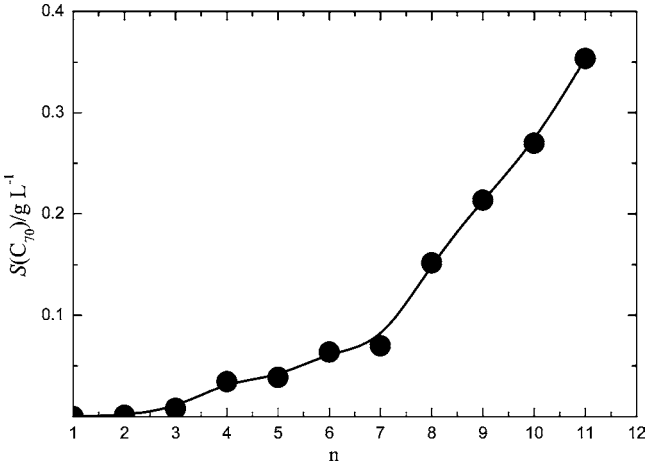

Figure 2. Solubility of the C_{70} fullerene in the homological series of 1-alkanoic carboxylic acid $C_nH_{2n+1}COOH$ (*n*, number of the carbon atoms in the hydrocarbon chain) at $T = 293$ K.

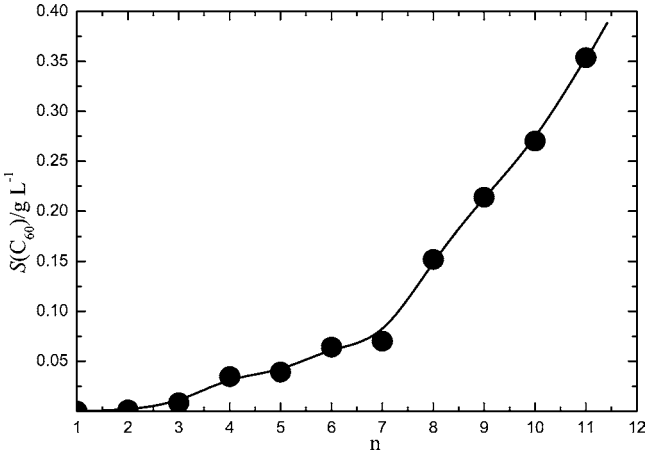

Figure 3. Solubility of the C_{60} fullerene in the homological series of alkan-1-ols $C_nH_{2n+1}OH$ (*n*, number of the carbon atoms in the hydrocarbon chain) at $T = 293$ K.

concentration of the C_{70} fullerene increases with the increase of the C_{60} fullerene concentration correspondingly (Figure 7).

Phase Equilibria in the Binary Systems Consisting of an Individual Light Fullerene and a Solvent. The process of a fullerene dissolution involves several stages. These stages are accompanied with the following energy effects: endothermic destruction of the fullerite lattice, breaking of

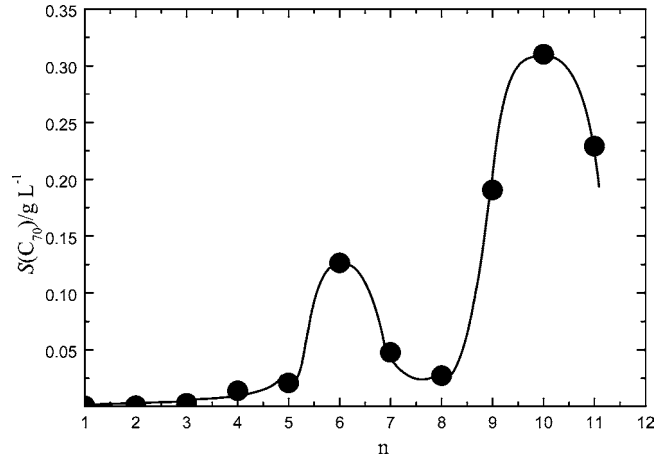

Figure 4. Solubility of the C_{70} fullerene in the homological series of alkan-1-ols $C_nH_{2n+1}OH$ (*n*, number of the carbon atoms in the hydrocarbon chain) at $T = 293$ K.

Table 3. Solubility of Light Fullerenes (C_{60} and C_{70}) in Oleic, Oleinic, And Linolenic Acids

T/K	*S*/g·L^{-1}	*T*/K	*S*/g·L^{-1}
C_{60} + oleic acid		C_{70} + oleic acid	
293.15	0.109	293.15	1.667
303.15	0.136	303.15	1.748
313.15	0.193	313.15	1.999
323.15	0.219	323.15	2.040
333.15	0.340	333.15	2.077
343.15	0.404	343.15	2.278
353.15	0.678	353.15	2.612
C_{60} + oleinic acid		C_{70} + oleinic acid	
293.15	0.244	293.15	1.867
303.15	0.315	303.15	2.099
313.15	0.449	313.15	2.235
323.15	0.621	323.15	2.323
333.15	0.733	333.15	2.411
343.15	1.109	343.15	2.919
353.15	1.486	353.15	3.526
C_{60} + linolenic acid		C_{70} + linolenic acid	
293.15	0.442	293.15	2.804
303.15	0.458	303.15	2.942
313.15	0.572	313.15	3.070
323.15	0.917	323.15	3.202
333.15	1.425	333.15	3.866
343.15	2.361	343.15	5.111
353.15	3.035	353.15	5.349

solvent−solvent bonds, as well as compensative effects of exothermic solvation process.[54] When the potential energies of solvent and solute molecules in the electrostatic field of solution are similar (Semenchenko's rule), the solubility of a solute reaches its maximum because of strong solute−solvent interactions.[55] Consequently, a fullerene dissolution enthalpy is the difference between the energy of fullerene solvation and the sum of energy expended in destroying of the fullerite lattice and breaking of solvent−solvent bonds. It should be noted that in contrast to nonpolar organic compounds the enthalpy of dissolution of the C_{60} is negative (exothermic effect of dissolution). Therefore, one can use the van't Hoff equation that describes the temperature dependence of solubility to show a decrease in solubility with an increase in temperature that is particularly atypical for nonelectrolytes. This decrease in solubility occurs after a solubility maximum in which a phase transition of the fullerene of the first order takes place. Such transition is caused by the destruction of a fullerene solvation sphere (see Figure 9).[56] Such dependences were described in the work of Ruoff[40] for the binary systems C_{60} + hexane, C_{60} + toluene, and C_{60} + carbon disulfide.

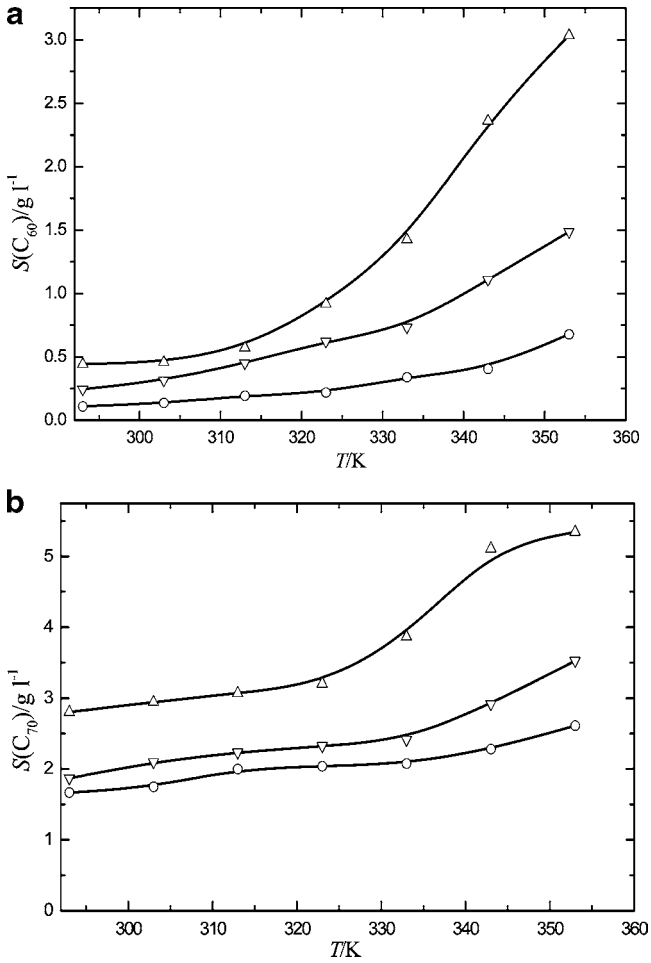

Figure 5. Solubility of individual light fullerenes C_{60} (a) and C_{70} (b) in oleic, linolic, and octadecatrienoic acids in the temperature range (293 to 353) K. ○, oleic acid; Δ, linolic acid; ∇, octadecatrienoic acid.

Table 4. Temperature Dependences of Solubility of the Industrial Fullerene Mixture Solubility with Mass Fraction (60 to 65) % of C_{60} + (33 to 39) % of C_{70} + (1 to 2) % wt. of C_{76}−C_{90} in Oleic, Oleinic and Linolenic Acids[a]

	T/K						
solvent	293.15	303.15	313.15	323.15	333.15	343.15	353.15
	S/g·L^{-1}						
oleic acid	1.650	1.713	1.688	1.840	1.923	2.209	2.748
	1.215	1.277	1.844	1.903	2.467	2.648	3.075
oleinic acid	1.956	1.948	2.369	2.924	3.282	3.300	3.928
	1.711	1.899	2.015	2.063	2.117	2.431	3.044
linolenic acid	1.739	1.991	2.904	2.931	3.005	3.664	4.922
	2.157	2.517	2.787	2.859	2.931	3.576	5.376

[a] Upper values correspond to solubility of C_{60}, and lower values correspond to solubility of C_{70}, g·dm^{-3}.

Analysis of literature data shows that such temperature dependences are rather frequent and take place not only in the above-listed cases (see Table 6). Such a solubility temperature dependence is widespread for binary water + salt systems such as NaF + H_2O, CaF_2 + H_2O, NH_4HF_2 + H_2O, $ZrOCl_2$ + H_2O, $MgSO_3$ + H_2O, $CuSO_4$ + H_2O, and $Th(SO_4)_2$ + H_2O (see Figure 10).[60] A summary of the data on fullerene solid solvates is presented in Table 7. The solvates of fullerenes are the compounds with constant composition. They are formed of fullerene and solvent molecules; furthermore, the solvate should be precipitated to the solid phase. We also disseminate this concept to solvated solid solutions of fullerenes ($(C_{60})_x(C_{70})_{1-x}$·nS). The

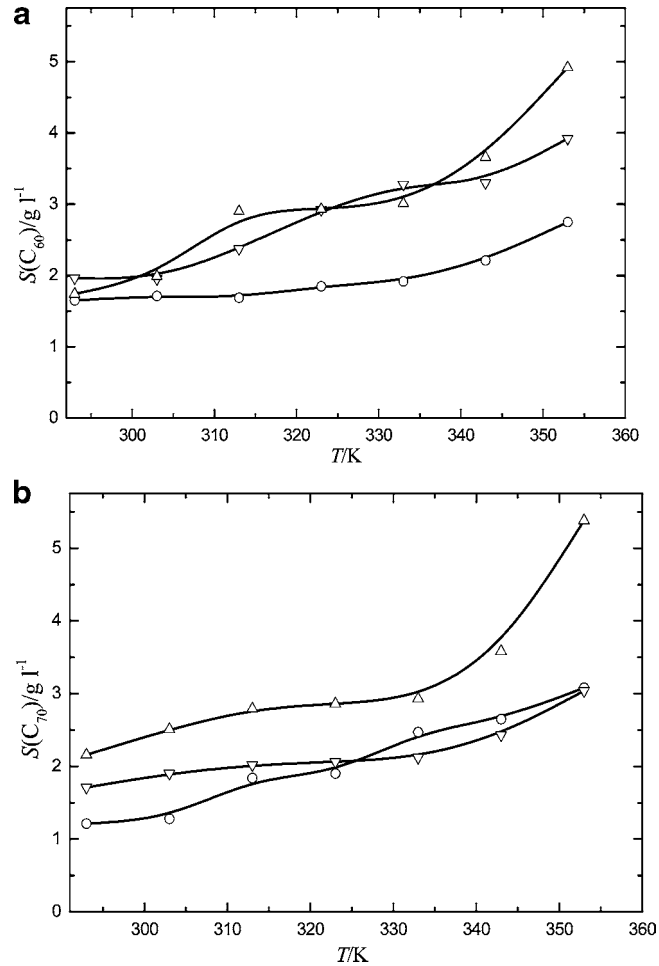

Figure 6. Solubility of the C_{60} fullerene (a) and C_{70} fullerene (b) from industrial fullerene mixture (65 % C_{60} + 34 % C_{70} + 1 % C_{76-90}) in oleic, linolic, and octadecatrienoic acids in the temperature range (293 to 353) K. ○, oleic acid; Δ, linolic acid; ∇, octadecatrienoic acid.

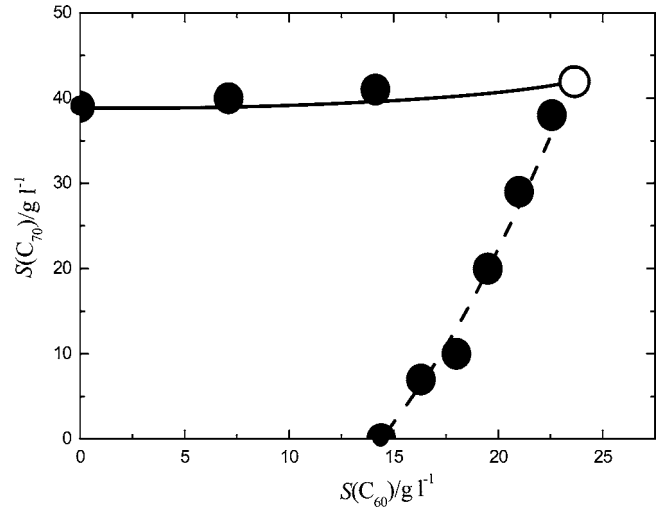

Figure 7. Solubility diagram in the ternary system C_{60} + C_{70} + $C_6H_4Cl_2$ at T = 423 K. Solid line corresponds to crystallization of $(C_{60})_x(C_{70})_{1-x}$ based on C_{60} fullerene; dashed line corresponds to crystallization of $(C_{60})_x(C_{70})_{1-x}$ based on C_{70} fullerene. $S(C_{60})$, the concentration of C_{60} in solution; $S(C_{70})$, the concentration of C_{70} in solution. "○" corresponds to simultaneous saturation of two solids.

fullerene's solvates are held together with weak van der Waals forces, and charge transfer was not detected by changes in infrared spectra. Some data on the stability of the solvated

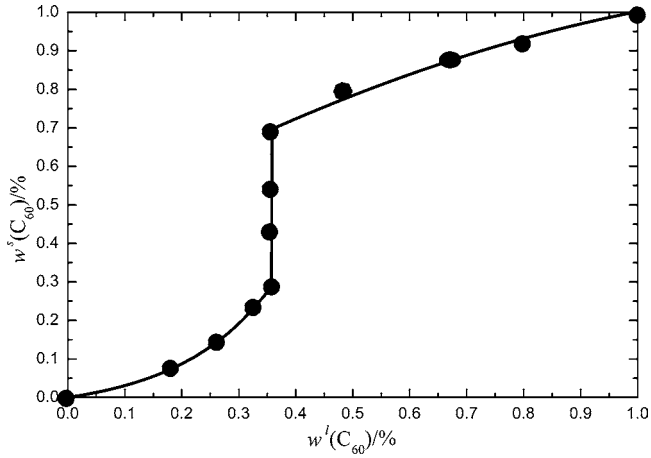

Figure 8. Fullerene component distribution between liquid and solid solutions in the ternary system $C_{60} + C_{70} + C_6H_4Cl_2$ at $T = 423$ K. $w^l(C_{60})$ is the mass fraction of the C_{60} fullerene in liquid solution; $w^s(C_{60})$ is the mass fraction of the C_{60} fullerene in solid solution.

Table 5. Equilibrium Liquid−Solid Phase Composition in the Ternary System $C_{60} + C_{70} + (o\text{-}C_6H_4Cl_2)$ at 423 K[a,b]

$S(C_{60})$/g·L^{-1}	$S(C_{70})$/g·L^{-1}	$w^l(C_{60})$/%	$w^s(C_{60})$/%	solid phase
14.4	0.00	1.000	1.000	C_{60}
16.4	6.90	0.796	0.918	$(C_{60})_x(C_{70})_{1-x}$ (1)
18.0	10.0	0.664	0.870	$(C_{60})_x(C_{70})_{1-x}$ (1)
19.6	19.9	0.477	0.783	$(C_{60})_x(C_{70})_{1-x}$ (1)
23.6	41.9	0.356	0.683	$(C_{60})_x(C_{70})_{1-x}$ (1) + $(C_{60})_x(C_{70})_{1-x}$ (2)
14.1	40.9	0.264	0.145	$(C_{60})_x(C_{70})_{1-x}$ (2)
7.19	40.0	0.182	0.076	$(C_{60})_x(C_{70})_{1-x}$ (2)
0.00	40.0	0.000	0.000	C_{70}

[a] (1), (2)-solid solutions enriched by C_{60} and C_{70} fullerenes correspondingly. [b] $S(C_{60})$, concentration of C_{60} in solution; $S(C_{70})$, 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.

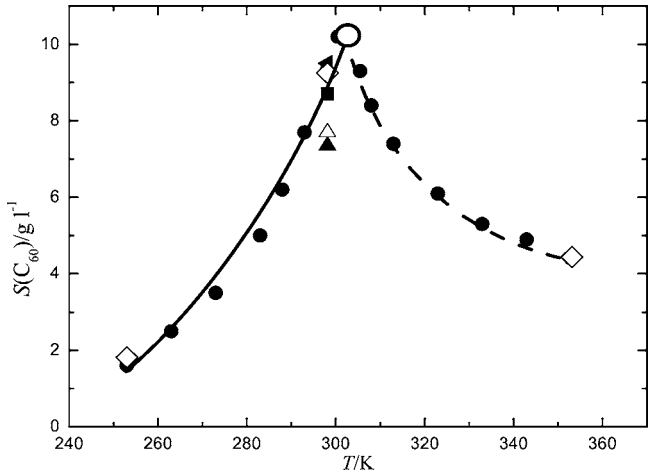

Figure 9. Solubility of the C_{60} fullerene in 1,2-dimethylbenzene. Solid line corresponds to crystallization of C_{60}·$2C_6H_4(CH_3)_2$; dashed line corresponds to crystallization of C_{60}. "○" is the dissociation point of bisolvated C_{60}·$2C_6H_4(CH_3)_2$ according to the reaction: C_{60}·$2C_6H_4(CH_3)_2$(solid) → C_{60}(solid) + $2C_6H_4(CH_3)_2$(liquid). ●, 18; ■, 15; ▲, 8; ○, 18; solid triangle pointing left, 19; Δ, 20; ◇, 50.

crystals of C_{60}, both measured by DSC and calculated through thermodynamic equations, are presented in ref 37.

The sigmoid shape[72] of the solubility temperature dependence (for example in the binary system C_{70} + 1,2-dimethylbenzene) is evidence of a nonsolvatic process of a fullerene dissolution (see Figure 11).

A thermodynamic model describing unusual temperature dependence of the solubility was proposed by Korobov. Thermodynamic equations derived show that the reason of anomalous solubility temperature dependence is the abnormal correlation between two enthalpies, namely, the enthalpy of solid solvate formation and the enthalpy of saturated liquid solution formation.[37,48,61,78] The model describes the equilibrium saturated solution of C_{60} + solid solvate on the low-temperature branch of the solubility curve up to the point of solubility maximum and saturated solution of C_{60} + solid individual C_{60} on the high-temperature branch of the solubility curve. Korobov's model assumes that fullerene solutions are infinitely diluted and simultaneously the composition dependence of activity coefficients can be neglected (this corresponds to Henry's law behavior).

A linear relation between logarithm of composition in saturated solution and inversed temperature was observed in a number of works;[40,18,21] this fact led them to conclude that enthalpy and entropy of the C_{60} dissolution are independent of composition and temperature (see Figure 12).

The constancy of activity coefficient was shown by Korobov by direct calculation using dissolution curves of C_{60} in toluene in the temperature range $T = (285$ to $383)$ K.[78] The existence of a linear relation between the logarithm of composition in saturated solution and inversed temperature can be used to examine calorimetric data on the basis of data obtained for dissolution curves.[78]

It has been found that there is no relationship between composition and partial molar volume of C_{60} for 12 organic solvents in a wide range of composition (from infinitely diluted to saturated solutions).[79] From the equation for partial molar volume of C_{60} in asymmetrical standardizing scale and taking into consideration that the standard state is the infinitely diluted solution (extrapolated value of partial molar volume to the point related to pure C_{60}), we can conclude that the standard state coincides with partial molar volume at infinite dilution.

$$V^{(l)}_{C_{60}} = V^{\infty}_{C_{60}} + RT\left(\frac{\partial \ln \gamma^{(l)}_{C_{60}}}{\partial p}\right)_T \qquad (3)$$

where $V(C_{60})$ is the partial molar volume of C_{60} in solution; $V^{\infty}(C_{60})$ is the partial molar volume of C_{60} at infinite dilution; γ_i is the activity coefficient of C_{60}; T is the absolute temperature (K); and R is the gas constant.

The absence of functional dependence between partial molar volume and composition can be observed only in two cases: $\gamma(C_{60}) = 1$ (the case of ideal solution) and $\gamma(C_{60}) =$ const in the whole composition range (the case of infinitely diluted solution).

It should be marked that dissolution of C_{60} is accompanied by a decrease of the molar volume of C_{60} compared with the solid crystalline phase. Ruelle et al. showed that the reason for such abnormal behavior for nonelectrolyte results from repulsion between π-orbitals which make molecules orientate themselves to diminish the repulsion effect from surrounding molecules.[79] Thus the repulsion prevents molecules from approaching each other and maintains them in equilibrium distance in the solid phase. This is not the case in solution. Sawamura et al. showed that the decrease of molar volume of C_{60} in the process of dissolution in toluene and hexane is the reason for the increase of solubility with an increase of pressure (see Table 8(a) and 8(b)).[38,80] The latest fact is a

Table 6. Temperature Dependences of Solubility of Light Fullerenes (C_{60} and C_{70}) in Various Solvents

Solubility of C_{60}							
solvent	T/K	S/g·L^{-1}	ref	solvent	T/K	S/g·L^{-1}	ref
hexane (C_6H_6)	195	0.006	40	benzene (C_6H_6)	298.1	0.89	24
hexane (C_6H_6)	238	0.017	40	benzene (C_6H_6)	308.1	0.97	24
hexane (C_6H_6)	273	0.038	40	benzene (C_6H_6)	328.1	1.22	24
hexane (C_6H_6)	283	0.066	40	benzene (C_6H_6)	338.1	1.46	24
hexane (C_6H_6)	288	0.055	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	253	1.6	18
hexane (C_6H_6)	298	0.049	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	263	2.5	18
hexane (C_6H_6)	318	0.039	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	273	3.5	18
hexane (C_6H_6)	338	0.039	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	283	5.0	18
toluene ($C_6H_5CH_3$)	195	0.1	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	288	6.2	18
toluene ($C_6H_5CH_3$)	233	0.75	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	293	7.7	18
toluene ($C_6H_5CH_3$)	243	0.96	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	298	9.3	18
toluene ($C_6H_5CH_3$)	248	1.3	40	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	300.5	10.2	18
toluene ($C_6H_5CH_3$)	253	1.5	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	303	10.3	18
		1.31	40				
toluene ($C_6H_5CH_3$)	258	1.9	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	305.5	9.3	18
toluene ($C_6H_5CH_3$)	263	2.5	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	308	8.4	18
toluene ($C_6H_5CH_3$)	268	3.2	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	313	7.4	18
toluene ($C_6H_5CH_3$)	273	4.0	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	323	6.1	18
		3.26	40				
toluene ($C_6H_5CH_3$)	278	3.9	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	333	5.3	18
toluene ($C_6H_5CH_3$)	278.2	3.59	38	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	343	4.9	18
toluene ($C_6H_5CH_3$)	283	3.7	18	1,2-dimethylbenzene ($C_6H_4(CH_3)_2$)	353	4.4	18
toluene ($C_6H_5CH_3$)	288	2.58	40	1,2-dichlorobenzene ($C_6H_4Cl_2$)	277.1	17.7	21
		2.68	40	1,2-dichlorobenzene ($C_6H_4Cl_2$)	288.1	18.4	21
toluene ($C_6H_5CH_3$)	288.2	3.15	38	1,2-dichlorobenzene ($C_6H_4Cl_2$)	293.1	20.8	21
toluene ($C_6H_5CH_3$)	293	3.3	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	295.1	21.0	21
toluene ($C_6H_5CH_3$)	295	2.86	40	1,2-dichlorobenzene ($C_6H_4Cl_2$)	295.6	21.1	21
toluene ($C_6H_5CH_3$)	298	2.9	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	298.1	7.12	24
		0.54	24				
		2.77	40				
toluene ($C_6H_5CH_3$)	298.15	2.45	43	1,2-dichlorobenzene ($C_6H_4Cl_2$)	298.15	27.13	42
toluene ($C_6H_5CH_3$)	298.2	2.80	38	1,2-dichlorobenzene ($C_6H_4Cl_2$)	304.1	25.7	21
toluene ($C_6H_5CH_3$)	303	2.7	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	308.1	8.60	24
toluene ($C_6H_5CH_3$)	308.1	0.62	24	1,2-dichlorobenzene ($C_6H_4Cl_2$)	308.1	23.34	42
toluene ($C_6H_5CH_3$)	308.15	2.24	43	1,2-dichlorobenzene ($C_6H_4Cl_2$)	309.1	26.7	21
toluene ($C_6H_5CH_3$)	308.2	2.53	38	1,2-dichlorobenzene ($C_6H_4Cl_2$)	310.1	26.8	21
toluene ($C_6H_5CH_3$)	313	2.24	40	1,2-dichlorobenzene ($C_6H_4Cl_2$)	318.1	9.69	24
		2.3	18				
toluene ($C_6H_5CH_3$)	318.15	2.11	43	1,2-dichlorobenzene ($C_6H_4Cl_2$)	318.15	15.04	42
toluene ($C_6H_5CH_3$)	323	2.2	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	319.1	24.4	21
toluene ($C_6H_5CH_3$)	328.1	0.82	24	1,2-dichlorobenzene ($C_6H_4Cl_2$)	325.1	18.7	21
toluene ($C_6H_5CH_3$)	328.15	2.03	43	1,2-dichlorobenzene ($C_6H_4Cl_2$)	328.1	11.4	24
toluene ($C_6H_5CH_3$)	333	1.9	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	328.15	12.28	42
toluene ($C_6H_5CH_3$)	338.1	1.02	24	1,2-dichlorobenzene ($C_6H_4Cl_2$)	333.1	12.6	24
toluene ($C_6H_5CH_3$)	338.15	1.90	43	1,2-dichlorobenzene ($C_6H_4Cl_2$)	336.1	16.3	21
toluene ($C_6H_5CH_3$)	343	1.8	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	338.15	14.08	24
toluene ($C_6H_5CH_3$)	353	1.5	18	1,2-dichlorobenzene ($C_6H_4Cl_2$)	346.1	15.5	21
		1.07	40				
toluene ($C_6H_5CH_3$)	383	0.88	40	1,2-dichlorobenzene ($C_6H_4Cl_2$)	352.1	13.95	21
thiophene (C_4H_4S)	298.1	0.25	24	1,2-dichlorobenzene ($C_6H_4Cl_2$)	367.1	11.5	21
thiophene (C_4H_4S)	308.1	0.28	24	1,2-dichlorobenzene ($C_6H_4Cl_2$)	378.1	10.4	21
thiophene (C_4H_4S)	318.1	0.34	24	1,2,4-trichlorobenzene ($C_6H_3Cl_3$)	298.1	4.83	24
thiophene (C_4H_4S)	328.1	0.50	24	1,2,4-trichlorobenzene ($C_6H_3Cl_3$)	308.1	5.70	24
tetrahydrothiophene (C_4H_8S)	298.1	0.12	24	1,2,4-trichlorobenzene ($C_6H_3Cl_3$)	318.1	6.90	24
tetrahydrothiophene (C_4H_8S)	308.1	0.14	24	1,2,4-trichlorobenzene ($C_6H_3Cl_3$)	328.1	8.00	24
tetrahydrothiophene (C_4H_8S)	318.1	0.20	24	1,2,4-trichlorobenzene ($C_6H_3Cl_3$)	333.1	8.86	24
tetrahydrothiophene (C_4H_8S)	328.1	0.25	24	carbon disulfide (CS_2)	195	>0.12	4
tetrahydrofuran (C_4H_8O)	298.1	0.06	24	carbon disulfide (CS_2)	238	0.72	40
tetrahydrofuran (C_4H_8O)	303.1	0.12	24	carbon disulfide (CS_2)	248	1.40	18
tetrahydrofuran (C_4H_8O)	308.1	0.17	24	carbon disulfide (CS_2)	253	5.97	40
tetrahydrofuran (C_4H_8O)	313.1	0.23	24	carbon disulfide (CS_2)	258	3.10	18
tetrahydrofuran (C_4H_8O)	318.1	0.32	24	carbon disulfide (CS_2)	263	4.70	18
tetrahydrofuran (C_4H_8O)	328.1	0.51	24	carbon disulfide (CS_2)	268	6.60	18
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	297.1	1.45	21	carbon disulfide (CS_2)	273	8.60	18
						7.17	40
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	313.1	1.70	21	carbon disulfide (CS_2)	278	8.10	18
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	338.1	2.11	21	carbon disulfide (CS_2)	283	8.20	18
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	359.1	2.90	21	carbon disulfide (CS_2)	288	6.69	40
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	383.1	3.42	21	carbon disulfide (CS_2)	293	8.00	18
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	397.1	3.74	21	carbon disulfide (CS_2)	298	7.70	18
						7.88	40
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	409.1	3.96	21	carbon disulfide (CS_2)	303	7.70	18
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	424.1	3.65	21	carbon disulfide (CS_2)	308	7.60	18
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	450.1	3.47	21	carbon disulfide (CS_2)	313	7.70	18

Table 6. Continued

Solubility of C_{60}							
solvent	*T*/K	S/g·L^{-1}	ref	solvent	*T*/K	S/g·L^{-1}	ref
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	466.1	3.13	21	carbon disulfide (CS_2)	318	6.45	40
1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	473.1	2.86	21	carbon disulfide (CS_2)	318	5.14	40
n-butylamine ($C_4H_9NH_2$)	298.1	3.69	24	carbon disulfide (CS_2)	318	4.90	40
n-butylamine ($C_4H_9NH_2$)	308.1	1.44	24	tetralin ($C_{10}H_{12}$)	293.2	13.7	21
n-butylamine ($C_4H_9NH_2$)	318.1	1.23	24	tetralin ($C_{10}H_{12}$)	294.2	14.2	21
butanoic acid ($C_4H_8O_2$)	293.15	0.01	57	tetralin ($C_{10}H_{12}$)	295.2	14.5	21
butanoic acid ($C_4H_8O_2$)	303.15	0.016	57	tetralin ($C_{10}H_{12}$)	307.2	15.2	21
butanoic acid ($C_4H_8O_2$)	313.15	0.018	57	tetralin ($C_{10}H_{12}$)	321.2	17.5	21
butanoic acid ($C_4H_8O_2$)	323.15	0.019	57	tetralin ($C_{10}H_{12}$)	329.2	21.5	21
butanoic acid ($C_4H_8O_2$)	333.15	0.020	57	tetralin ($C_{10}H_{12}$)	335.2	21.2	21
butanoic acid ($C_4H_8O_2$)	343.15	0.031	57	tetralin ($C_{10}H_{12}$)	338.2	20.0	21
butanoic acid ($C_4H_8O_2$)	353.15	0.033	57	tetralin ($C_{10}H_{12}$)	340.2	19.6	21
hexanoic acid ($C_6H_{12}O_2$)	293.15	0.184	58	tetralin ($C_{10}H_{12}$)	351.2	19.0	21
hexanoic acid ($C_6H_{12}O_2$)	303.15	0.197	58	tetralin ($C_{10}H_{12}$)	360.2	14.6	21
hexanoic acid ($C_6H_{12}O_2$)	313.15	0.186	58	pentanoic acid ($C_5H_{10}O_2$)	293.15	0.058	58
hexanoic acid ($C_6H_{12}O_2$)	323.15	0.170	58	pentanoic acid ($C_5H_{10}O_2$)	303.15	0.065	58
hexanoic acid ($C_6H_{12}O_2$)	333.15	0.146	58	pentanoic acid ($C_5H_{10}O_2$)	313.15	0.068	58
hexanoic acid ($C_6H_{12}O_2$)	343.15	0.135	58	pentanoic acid ($C_5H_{10}O_2$)	323.15	0.071	58
hexanoic acid ($C_6H_{12}O_2$)	353.15	0.127	58	pentanoic acid ($C_5H_{10}O_2$)	333.15	0.086	58
octanoic acid ($C_8H_{16}O_2$)	293.15	0.047	59	pentanoic acid ($C_5H_{10}O_2$)	343.15	0.080	58
octanoic acid ($C_8H_{16}O_2$)	303.15	0.050	59	pentanoic acid ($C_5H_{10}O_2$)	353.15	0.070	58
octanoic acid ($C_8H_{16}O_2$)	313.15	0.060	59	heptanoic acid ($C_7H_{14}O_2$)	293.15	0.279	57
octanoic acid ($C_8H_{16}O_2$)	323.15	0.068	59	heptanoic acid ($C_7H_{14}O_2$)	303.15	0.276	57
octanoic acid ($C_8H_{16}O_2$)	333.15	0.056	59	heptanoic acid ($C_7H_{14}O_2$)	313.15	0.269	57
octanoic acid ($C_8H_{16}O_2$)	343.15	0.052	59	heptanoic acid ($C_7H_{14}O_2$)	323.15	0.254	57
octanoic acid ($C_8H_{16}O_2$)	353.15	0.043	59	heptanoic acid ($C_7H_{14}O_2$)	333.15	0.271	57
nonanoic acid ($C_9H_{18}O_2$)	293.15	0.161	59	heptanoic acid ($C_7H_{14}O_2$)	343.15	0.287	57
nonanoic acid ($C_9H_{18}O_2$)	303.15	0.176	59	heptanoic acid ($C_7H_{14}O_2$)	353.15	0.321	57
nonanoic acid ($C_9H_{18}O_2$)	313.15	0.185	59	hexan-1-ol ($C_6H_{13}OH$)	293.15	0.064	13
nonanoic acid ($C_9H_{18}O_2$)	323.15	0.228	59	hexan-1-ol ($C_6H_{13}OH$)	303.15	0.033	13
nonanoic acid ($C_9H_{18}O_2$)	333.15	0.225	59	hexan-1-ol ($C_6H_{13}OH$)	313.15	0.060	13
nonanoic acid ($C_9H_{18}O_2$)	343.15	0.217	59	hexan-1-ol ($C_6H_{13}OH$)	323.15	0.059	13
nonanoic acid ($C_9H_{18}O_2$)	353.15	0.213	59	hexan-1-ol ($C_6H_{13}OH$)	333.15	0.066	13
pentan-1-ol ($C_5H_{11}OH$)	293.15	0.039	13	hexan-1-ol ($C_6H_{13}OH$)	343.15	0.076	13
pentan-1-ol ($C_5H_{11}OH$)	303.15	0.030	13	hexan-1-ol ($C_6H_{13}OH$)	353.15	0.087	13
pentan-1-ol ($C_5H_{11}OH$)	313.15	0.037	13	heptan-1-ol ($C_7H_{15}OH$)	293.15	0.069	13
pentan-1-ol ($C_5H_{11}OH$)	323.15	0.041	13	heptan-1-ol ($C_7H_{15}OH$)	303.15	0.056	13
pentan-1-ol ($C_5H_{11}OH$)	333.15	0.043	13	heptan-1-ol ($C_7H_{15}OH$)	313.15	0.061	13
pentan-1-ol ($C_5H_{11}OH$)	343.15	0.045	13	heptan-1-ol ($C_7H_{15}OH$)	323.15	0.073	13
pentan-1-ol ($C_5H_{11}OH$)	353.15	0.047	13	heptan-1-ol ($C_7H_{15}OH$)	333.15	0.076	13
octan-1-ol ($C_8H_{17}OH$)	293.15	0.152	13	heptan-1-ol ($C_7H_{15}OH$)	343.15	0.080	13
octan-1-ol ($C_8H_{17}OH$)	303.15	0.146	13	heptan-1-ol ($C_7H_{15}OH$)	353.15	0.086	13
octan-1-ol ($C_8H_{17}OH$)	313.15	0.144	13	nonan-1-ol ($C_9H_{19}OH$)	293.15	0.214	13
octan-1-ol ($C_8H_{17}OH$)	323.15	0.138	13	nonan-1-ol ($C_9H_{19}OH$)	303.15	0.218	13
octan-1-ol ($C_8H_{17}OH$)	333.15	0.145	13	nonan-1-ol ($C_9H_{19}OH$)	313.15	0.222	13
octan-1-ol ($C_8H_{17}OH$)	343.15	0.149	13	nonan-1-ol ($C_9H_{19}OH$)	323.15	0.227	13
octan-1-ol ($C_8H_{17}OH$)	353.15	0.150	13	nonan-1-ol ($C_9H_{19}OH$)	333.15	0.231	13
decan-1-ol ($C_{10}H_{21}OH$)	293.15	0.270	13	nonan-1-ol ($C_9H_{19}OH$)	343.15	0.248	13
decan-1-ol ($C_{10}H_{21}OH$)	303.15	0.291	13	nonan-1-ol ($C_9H_{19}OH$)	353.15	0.283	13
decan-1-ol ($C_{10}H_{21}OH$)	313.15	0.301	13	undecan-1-ol ($C_{11}H_{23}OH$)	293.15	0.354	13
decan-1-ol ($C_{10}H_{21}OH$)	323.15	0.283	13	undecan-1-ol ($C_{11}H_{23}OH$)	303.15	0.377	13
decan-1-ol ($C_{10}H_{21}OH$)	333.15	0.249	13	undecan-1-ol ($C_{11}H_{23}OH$)	313.15	0.388	13
decan-1-ol ($C_{10}H_{21}OH$)	343.15	0.240	13	undecan-1-ol ($C_{11}H_{23}OH$)	323.15	0.400	13
decan-1-ol ($C_{10}H_{21}OH$)	353.15	0.206	13	undecan-1-ol ($C_{11}H_{23}OH$)	333.15	0.330	13
heptane (C_7H_{16})	273.15	0.025	6	undecan-1-ol ($C_{11}H_{23}OH$)	343.15	0.306	13
heptane (C_7H_{16})	293.15	0.027	6	undecan-1-ol ($C_{11}H_{23}OH$)	353.15	0.284	13
heptane (C_7H_{16})	303.15	0.032	6	styrene ($C_6H_5CH{=}CH_2$)	258.15	5.90	25
heptane (C_7H_{16})	313.15	0.040	6	styrene ($C_6H_5CH{=}CH_2$)	273.15	5.55	25
heptane (C_7H_{16})	323.15	0.035	6	styrene ($C_6H_5CH{=}CH_2$)	293.15	4.02	25
heptane (C_7H_{16})	333.15	0.038	6	styrene ($C_6H_5CH{=}CH_2$)	303.15	4.18	25
heptane (C_7H_{16})	343.15	0.044	6	styrene ($C_6H_5CH{=}CH_2$)	313.15	4.82	25
heptane (C_7H_{16})	353.15	0.044	6	styrene ($C_6H_5CH{=}CH_2$)	323.15	4.18	25
				styrene ($C_6H_5CH{=}CH_2$)	333.15	3.95	25
				styrene ($C_6H_5CH{=}CH_2$)	343.15	3.83	25
Solubility of C_{70}							
toluene ($C_6H_5CH_3$)	233	1.3	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	253	5.6	18
toluene ($C_6H_5CH_3$)	253	1.3	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	263	6.8	18
toluene ($C_6H_5CH_3$)	273	1.3	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	273	9.8	18
toluene ($C_6H_5CH_3$)	283	1.4	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	283	13.1	18
toluene ($C_6H_5CH_3$)	293	1.5	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	293	16.6	18
toluene($C_6H_5CH_3$)	298	1.5	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	298	15.6	18
		1.07	17				
		1.406	46				
toluene ($C_6H_5CH_3$)	313	1.6	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	313	18.2	18

Table 6. Continued

Solubility of C_{60}							
solvent	T/K	S/g·L^{-1}	ref	solvent	T/K	S/g·L^{-1}	ref
toluene ($C_6H_5CH_3$)	333	1.6	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	333	20.7	18
toluene ($C_6H_5CH_3$)	353	1.7	18	1,2-dimethylbenzene ($(C_6H_4(CH_3)_2$)	353	21.8	18
carbon disulfide (CS_2)	233	6.0	18	tetralin ($C_{10}H_{12}$)	277.1	10.2	21
carbon disulfide (CS_2)	253	7.7	18	tetralin ($C_{10}H_{12}$)	293.1	11.7	21
carbon disulfide (CS_2)	263	9.5	18	tetralin ($C_{10}H_{12}$)	294.1	11.9	21
carbon disulfide (CS_2)	273	11.1	18	tetralin ($C_{10}H_{12}$)	295.1	12.1	21
carbon disulfide (CS_2)	283	12.8	18	tetralin ($C_{10}H_{12}$)	298	12.3	21
carbon disulfide (CS_2)	293	14.4	18	tetralin ($C_{10}H_{12}$)	301.1	12.4	21
carbon disulfide (CS_2)	298	15.3	18	tetralin ($C_{10}H_{12}$)	310.1	14.4	21
		9.875	46				
		10.16	17				
1,2-dichlorobenzen ($C_6H_4Cl_2$)	292.1	23.4	21	tetralin ($C_{10}H_{12}$)	315.1	16.5	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	293.1	24.4	21	tetralin ($C_{10}H_{12}$)	321.1	17.4	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	294.1	25.5	21	tetralin ($C_{10}H_{12}$)	329.1	16.7	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	298	36.21	52	tetralin ($C_{10}H_{12}$)	338.1	16.0	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	312.1	27.7	21	tetralin ($C_{10}H_{12}$)	351.1	13.4	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	321.1	33.9	21	tetralin ($C_{10}H_{12}$)	360.1	11.7	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	323.1	36.0	21	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	292.1	1.86	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	328.1	38.3	21	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	297.1	1.45	37
1,2-dichlorobenzene ($C_6H_4Cl_2$)	337.1	36.9	21	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	303.1	2.69	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	342.1	28.8	21	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	310.1	2.87	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	347.1	27.5	21	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	314.1	3.21	21
1,2-dichlorobenzene ($C_6H_4Cl_2$)	359.1	26.3	21	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	316.6	3.18	21
butanoic acid ($C_4H_8O_2$)	293.15	0.013	51	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	320.1	2.75	21
butanoic acid ($C_4H_8O_2$)	303.15	0.016	51	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	328.1	2.19	21
butanoic acid ($C_4H_8O_2$)	313.15	0.019	51	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	334.1	2.13	21
butanoic acid ($C_4H_8O_2$)	323.15	0.022	51	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	339.1	1.96	21
butanoic acid ($C_4H_8O_2$)	333.15	0.037	51	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	351.1	1.56	21
butanoic acid ($C_4H_8O_2$)	343.15	0.036	51	1,3-diphenylacetone ($(C_6H_5CH_2)_2CO$)	361.1	1.44	21
butanoic acid ($C_4H_8O_2$)	353.15	0.048	51	hexanoic acid ($C_6H_{12}O_2$)	293.15	0.125	51
pentanoic acid ($C_5H_{10}O_2$)	293.15	0.013	51	hexanoic acid ($C_6H_{12}O_2$)	303.15	0.131	51
pentanoic acid ($C_5H_{10}O_2$)	303.15	0.020	51	hexanoic acid ($C_6H_{12}O_2$)	313.15	0.140	51
pentanoic acid ($C_5H_{10}O_2$)	313.15	0.022	51	hexanoic acid ($C_6H_{12}O_2$)	323.15	0.146	51
pentanoic acid ($C_5H_{10}O_2$)	323.15	0.026	51	hexanoic acid ($C_6H_{12}O_2$)	333.15	0.150	51
pentanoic acid ($C_5H_{10}O_2$)	333.15	0.031	51	hexanoic acid ($C_6H_{12}O_2$)	343.15	0.150	51
pentanoic acid ($C_5H_{10}O_2$)	343.15	0.033	51	hexanoic acid ($C_6H_{12}O_2$)	353.15	0.154	51
pentanoic acid ($C_5H_{10}O_2$)	353.15	0.039	51	octanoic acid ($C_8H_{16}O_2$)	293.15	0.110	51
heptanoic acid ($C_7H_{14}O_2$)	293.15	0.330	51	octanoic acid ($C_8H_{16}O_2$)	303.15	0.135	51
heptanoic acid ($C_7H_{14}O_2$)	303.15	0.357	51	octanoic acid ($C_8H_{16}O_2$)	313.15	0.152	51
heptanoic acid ($C_7H_{14}O_2$)	313.15	0.380	51	octanoic acid ($C_8H_{16}O_2$)	323.15	0.153	51
heptanoic acid ($C_7H_{14}O_2$)	323.15	0.381	51	octanoic acid ($C_8H_{16}O_2$)	333.15	0.154	51
heptanoic acid ($C_7H_{14}O_2$)	333.15	0.400	51	octanoic acid ($C_8H_{16}O_2$)	343.15	0.154	51
heptanoic acid ($C_7H_{14}O_2$)	343.15	0.447	51	octanoic acid ($C_8H_{16}O_2$)	353.15	0.166	51
heptanoic acid ($C_7H_{14}O_2$)	353.15	0.439	51	nonanoic acid ($C_9H_{18}O_2$)	293.15	0.056	51
butan-1-ol (C_4H_9OH)	293.15	0.014	52	nonanoic acid ($C_9H_{18}O_2$)	303.15	0.057	51
butan-1-ol (C_4H_9OH)	303.15	0.014	52	nonanoic acid ($C_9H_{18}O_2$)	313.15	0.058	51
butan-1-ol (C_4H_9OH)	313.15	0.016	52	nonanoic acid ($C_9H_{18}O_2$)	323.15	0.057	51
butan-1-ol (C_4H_9OH)	323.15	0.019	52	nonanoic acid ($C_9H_{18}O_2$)	333.15	0.084	51
butan-1-ol (C_4H_9OH)	333.15	0.019	52	nonanoic acid ($C_9H_{18}O_2$)	343.15	0.101	51
butan-1-ol (C_4H_9OH)	343.15	0.019	52	nonanoic acid ($C_9H_{18}O_2$)	353.15	0.117	51
butan-1-ol (C_4H_9OH)	353.15	0.023	52	hexan-1-ol ($C_6H_{13}OH$)	293.15	0.126	52
pentan-1-ol ($C_5H_{11}OH$)	293.15	0.021	52	hexan-1-ol ($C_6H_{13}OH$)	303.15	0.129	52
pentan-1-ol ($C_5H_{11}OH$)	303.15	0.022	52	hexan-1-ol ($C_6H_{13}OH$)	313.15	0.131	52
pentan-1-ol ($C_5H_{11}OH$)	313.15	0.026	52	hexan-1-ol ($C_6H_{13}OH$)	323.15	0.142	52
pentan-1-ol ($C_5H_{11}OH$)	323.15	0.027	52	hexan-1-ol ($C_6H_{13}OH$)	333.15	0.153	52
pentan-1-ol ($C_5H_{11}OH$)	333.15	0.027	52	hexan-1-ol ($C_6H_{13}OH$)	343.15	0.175	52
pentan-1-ol ($C_5H_{11}OH$)	343.15	0.028	52	hexan-1-ol ($C_6H_{13}OH$)	353.15	0.219	52
pentan-1-ol ($C_5H_{11}OH$)	353.15	0.028	52	heptan-1-ol ($C_7H_{15}OH$)	293.15	0.046	52
octan-1-ol ($C_8H_{17}OH$)	293.15	0.027	52	heptan-1-ol ($C_7H_{15}OH$)	303.15	0.057	52
octan-1-ol ($C_8H_{17}OH$)	303.15	0.031	52	heptan-1-ol ($C_7H_{15}OH$)	313.15	0.054	52
octan-1-ol ($C_8H_{17}OH$)	313.15	0.034	52	heptan-1-ol ($C_7H_{15}OH$)	323.15	0.058	52
octan-1-ol ($C_8H_{17}OH$)	323.15	0.041	52	heptan-1-ol ($C_7H_{15}OH$)	333.15	0.061	52
octan-1-ol ($C_8H_{17}OH$)	333.15	0.044	52	heptan-1-ol ($C_7H_{15}OH$)	343.15	0.071	52
octan-1-ol ($C_8H_{17}OH$)	343.15	0.048	52	heptan-1-ol ($C_7H_{15}OH$)	353.15	0.115	52
octan-1-ol ($C_8H_{17}OH$)	353.15	0.054	52	nonan-1-ol ($C_9H_{19}OH$)	293.15	0.190	52
decan-1-ol ($C_{10}H_{21}OH$)	293.15	0.310	52	nonan-1-ol ($C_9H_{19}OH$)	303.15	0.204	52
decan-1-ol ($C_{10}H_{21}OH$)	303.15	0.299	52	nonan-1-ol ($C_9H_{19}OH$)	313.15	0.238	52
decan-1-ol ($C_{10}H_{21}OH$)	313.15	0.294	52	nonan-1-ol ($C_9H_{19}OH$)	323.15	0.258	52
decan-1-ol ($C_{10}H_{21}OH$)	323.15	0.294	52	nonan-1-ol ($C_9H_{19}OH$)	333.15	0.257	52
decan-1-ol ($C_{10}H_{21}OH$)	333.15	0.293	52	nonan-1-ol ($C_9H_{19}OH$)	343.15	0.258	52
decan-1-ol ($C_{10}H_{21}OH$)	343.15	0.283	52	nonan-1-ol ($C_9H_{19}OH$)	353.15	0.264	52
decan-1-ol ($C_{10}H_{21}OH$)	353.15	0.283	52	undecan-1-ol ($C_{11}H_{23}OH$)	293.15	0.229	52
styrene ($C_6H_5CH{=}CH_2$)	258.15	2.95	25	undecan-1-ol ($C_{11}H_{23}OH$)	303.15	0.237	52
styrene ($C_6H_5CH{=}CH_2$)	273.15	5.60	25	undecan-1-ol ($C_{11}H_{23}OH$)	313.15	0.326	52

Table 6. Continued

Solubility of C_{60}							
solvent	*T*/K	S/g·L^{-1}	ref	solvent	*T*/K	S/g·L^{-1}	ref
styrene ($C_6H_5CH{=}CH_2$)	293.15	4.72	25	undecan-1-ol ($C_{11}H_{23}OH$)	323.15	0.328	52
styrene ($C_6H_5CH{=}CH_2$)	303.15	5.01	25	undecan-1-ol ($C_{11}H_{23}OH$)	333.15	0.314	52
styrene ($C_6H_5CH{=}CH_2$)	313.15	7.35	25	undecan-1-ol ($C_{11}H_{23}OH$)	343.15	0.314	52
styrene ($C_6H_5CH{=}CH_2$)	323.15	7.88	25	undecan-1-ol ($C_{11}H_{23}OH$)	353.15	0.314	52
styrene ($C_6H_5CH{=}CH_2$)	333.15	8.14	25	heptane (C_7H_{16})	273.15	0.021	6
styrene ($C_6H_5CH{=}CH_2$)	343.15	9.71	25	heptane (C_7H_{16})	293.15	0.031	6
styrene ($C_6H_5CH{=}CH_2$)	353.15	9.84	25	heptane (C_7H_{16})	303.15	0.032	6
				heptane (C_7H_{16})	313.15	0.039	6
				heptane (C_7H_{16})	323.15	0.041	6
				heptane (C_7H_{16})	333.15	0.039	6
				heptane (C_7H_{16})	343.15	0.039	6
				heptane (C_7H_{16})	353.15	0.057	6

direct consequence from Planck−van-Laar's equation for infinitely diluted solutions

$$\left(\frac{d \ln x_{C_{60}}^{(l)}}{dp}\right)_T = -\frac{\Delta V}{RT} \quad (4)$$

Actually, the Planck−van-Laar equation in the above form can be used for the description of pressure effect on solubility of the C_{60} fullerene since the dependence of logarithm of the C_{60} fullerene mole fraction in the saturated solution as a function of pressure is linear (see Figure 13). This fact is additional evidence that a fullerene activity coefficient is constant in a saturated solution.

While studying the solubility of light fullerenes in various solvents, particular attention has been paid to searching for correlations between solubility and various molecular characteristics of the solvents. Sivarman et al. determined the solubility of C_{60} in 15 polar and nonpolar solvents and discussed a correlation between solubility and Hildebrand's solubility parameter (molecular characteristic of solvent−solvent and solute−solute interactions) determined by[2,81]

$$\delta = [(\Delta_{vap}H - RT)/V]^{1/2} \quad (5)$$

where $\Delta_{vap}H$ is the molar enthalpy of vaporization; T is the temperature; V is the molar volume, and R is the gas constant.

As a result, Sivarman et al. showed that solubility reaches its maximum when the Hildebrand solubility parameters for solute and for solvent are similar.[2] According to Hildebrand's theory, solubility parameters are determined only for the liquid state, and in the case of fullerene, the standard state corresponds to hypothetical supercooled liquid of fullerene. Later, Ruoff et al. showed that to determine the Hildebrand cohesion parameter one can replace the enthalpy of vaporation by the sublimation enthalpy.[1,53] Ruoff et al. also demonstrated that there are no molecular parameters which can universally predict the solubility of fullerenes; however, they determined a set of solvent parameters which can predict well fullerene solubility.[1] These solvent characteristics are the following: high value of refraction index; value of dielectric permittivity equal to 4; high molecular volume of the solvent; value of Hildebrand's solubility parameter equal to 20 $[J/cm^3]^{1/2}$; nucleophilic properties of a solvent.

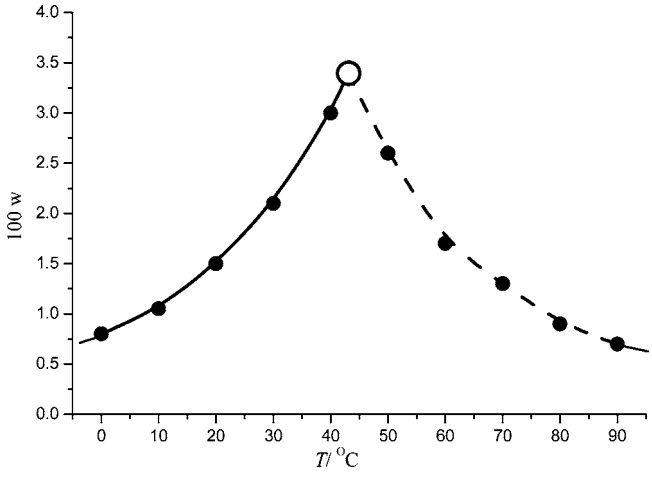

Figure 10. Solubility of the $Th(SO_4)_2$ in water. Solid line corresponds to crystallization of $Th(SO_4)_2 \cdot 9\ H_2O$; dashed line corresponds to crystallization of $Th(SO_4)_2 \cdot 4\ H_2O$. "○" is the dissociation point of bisolvated $Th(SO_4)_2 \cdot 9H_2O$ according to the reaction: $Th(SO_4)_2 \cdot 9H_2O(solid) \rightarrow Th(SO_4)_2 \cdot 4H_2O(solid) + 5H_2O(liquid)$.

The fundamental characteristics of fullerene molecules are the first electron affinity (EA) and the first ionization energy (IE). For C_{60} EA = $(4.273 \pm 0.002) \cdot 10^{-19}$ J and IE = $(12.13 \pm 0.02) \cdot 10^{-19}$ J.[82−84] Notable is that the value of electron affinity of C_{60} is higher than that of aromatic solvents. This illustrates the strong electron-acceptor properties of fullerenes. Herbst et al. investigated the dissolution enthalpies of the C_{60} in five solvents (benzene, toluene, brombenzene, 1,2,-dichlorobenzene, nitrobenzene).[54] Since fullerenes are the Lewis acids, one can expect more exothermic dissolving effect with increasing number of donor groups in the solvent molecule (due to more effective solvent−solute interaction).

Herbst et al. showed that not only the above-mentioned molecular characteristics of solvents but also a dissolution enthalpy can predict the solubility of fullerenes.[54]

Heyman used the Scatchard−Hildebrand regular solution model to describe solubility data of the C_{60} fullerene in alkanes, branched alkanes, 1-alkanols, branched alkanols, and diols.[3] The second-order polynomial dependence between solubility and Hildebrand's solubility parameter was determined on the basis of approximations of the theory and conditions of chemical equilibrium between C_{60} in the solid phase and saturated solution. However, the derived equation was suitable to describe only homologous series of alkanes. Korobov et al. marked that the model of regular solution cannot be used for describing solubility of fullerenes.[37] According to Skatchard−Hildebrand's equation, the model considers the cases only with positive excess enthalpy of solution and with zero excess entropy of solution.[85,86] In the case of dissolution of fullerene, the exothermic effect $\Delta_{diss}H < 0$ and $\Delta_{diss}S < 0$ and is smaller than the enthalpy. Thus, the dissolution of fullerene is controlled by the entropy process.

Phase Equilibria in the Ternary Systems. C_{60}−C_{70} Solvent. There are little data on the solubility of C_{60} and C_{70} fullerenes in the same solvent and the solubility of particular fullerenes in mixed solvents. Ponomarev et al.[50,96] investigated the solubility in ternary system $C_{60} + C_{70}$ + *o*-xylene at (253,

Table 7. Composition of Solid Solvates of C_{60} and C_{70}[a]

system fullerene + solvent (S)	T_{imp}/K[c]	solvate composition, $C_{60}\cdot nS$ (n, number of solvent molecules)	method[b]	ref.
		Solid Solvates of C_{60}		
C_{60} + bromobenzene	350 ± 1	2.0 ± 0.2[c]	TG	48
(C_{60} + C_6H_5Br)		2		61
C_{60} + 1,2-dibromobenzene	350.9 ± 1.1	2.9 ± 0.1	DSC	62
(C_{60} + 1,2-$C_6H_4Br_2$)				
C_{60} + 1,3-dibromobenzene	336.0 ± 5.1	1.9 ± 0.1	DSC	62, 44
(C_{60} + 1,3-$C_6H_4Br_2$)	484.4 ± 6.8	−		
C_{60} + benzene	322 ± 1	3.8 ± 0.2	TG	48
(C_{60} + C_6H_6)		4		64−66
C_{60} + toluene	285.0 ± 0.2	1.8 ± 0.2	TG	48, 63
(C_{60} + $C_6H_5CH_3$)	285 ± 1			
	331 ± 1			
C_{60} + 1,2-dimethylbenzene	318	2.0 to 3.4	TG	48
(C_{60} + 1,2-$C_6H_4(CH_3)_2$)	322.0 ± 2.6	2.1 ± 0.2		23
C_{60} + 1,2-dimethylbenzene	294.0 ± 1.0	2.3 to 3.6	TG	48
(C_{60} + 1,3-$C_6H_4(CH_3)_2$)	332.0 ± 1.2	0.6		63
	370.0 ± 3.7			
C_{60} + 1,2-dichlorobenzene	322	2.0 to 2.7	TG	48
(C_{60} + 1,2-$C_6H_4Cl_2$)	342	2.0 ± 0.5		
C_{60} + 1,3-dichlorobenzene	308.5 ± 1.3	2.3 ± 0.5	TG	48
(C_{60} + 1,3-$C_6H_4Cl_2$)	406 ± 3	0.6		63
C_{60} + 1,2,4-trichlorobenzene	340.3 ± 2.4	2.0 ± 0.1	DSC	44
C_{60} + 1,2,4-$C_6H_3Cl_3$				
C_{60} + 1,2-iodobenzene	384 (389)	2	DSC	63
(C_{60} + C_6H_5I)				
C_{60} + 1,3,5-trimethylbenzene	292 to 300	2.0 to 4.0	TG	67
(C_{60} + 1,3,5-$C_6H_3(CH_3)_3$)	296	0.5 ± 0.2		63
	460.8 ± 1.5			
C_{60} + 1,2,4-trimethylbenzene	322	1.7 to 2.4	TG	48
C_{60} + 1,2,4-$C_6H_3(CH_3)_3$				
C_{60} + 1,1-dichloroethane	343	1	TG	68
(C_{60} + 1,1-$C_2H_4Cl_2$)				
C_{60} + 1,2-dichloroethane	350	1	TGA	66
C_{60} + 1,2- $C_2H_4Cl_2$				
C_{60} + 1,1,2-trichloroethane	430	1	TG	68
(C_{60} + Cl_2H-CCH_2Cl)	436			
C_{60} + trichloroethylene	416	1	TG	68
(C_{60} + C_2HCl_3)				
C_{60} + hexane	383	1	TG	71
(C_{60} + C_6H_{14})				
C_{60} + heptane	383	1	TG	70
(C_{60} + C_7H_{16})				
C_{60} + octane	398	1	TG	73
(C_{60} + C_8H_{18})				
C_{60} + nonane	399	2/3	TG	70
(C_{60} + C_9H_{20})				
C_{60} + tetrachloromethane	319	13	TG	74, 75
(C_{60} + CCl_4)	402	2	TG	63
C_{60} + cyclohexane	350	13	TG	37
(C_{60} + C_6H_{12})		2		9
C_{60} + tribromomethane	−	2	TG	76
(C_{60} + $CHBr_3$)				
C_{60} + trichlorobromomethane	344	12	TG	77
(C_{60} + $BrCCl_3$)	407	2		
C_{60} + styrene	−	2	TG	25
(C_{60} + $C_6H_5CH{=}CH_2$)				
C_{60} + butiric acid	−	1	TG	57
(C_{60} + C_3H_7COOH)				
C_{60} + valeric acid	−	1	TG	58
(C_{60} + C_4H_9COOH)				
C_{60} + caproic acid	−	1	TG	58
(C_{60} + $C_5H_{11}COOH$)				
C_{60} + heptanoic acid	−	1	TG	57
(C_{60} + $C_6H_{13}COOH$)				
C_{60} + caprylic acid	−	1	TG	59
(C_{60} + $C_7H_{15}COOH$)				
C_{60} + pelargonic acid	−	1	TG	59
(C_{60} + $C_8H_{17}COOH$)				
C_{60} + *n*-pentanol	−	1	TG	13
(C_{60} + *n*-$C_5H_{11}OH$)				
C_{60} + *n*-hexanol	−	1	TG	13
(C_{60} + *n*-$C_6H_{13}OH$)				
C_{60} + *n*-heptanol	−	1	TG	13
(C_{60} + *n*-$C_7H_{15}OH$)				
C_{60} + *n*-octanol	−	1	TG	13
(C_{60} + *n*-$C_8H_{17}OH$)				

Table 7. Continued

system fullerene + solvent (S)	T_{imp}/K[c]	solvate composition, C_{60}·*n*S (*n*, number of solvent molecules)	method[b]	ref.
C_{60} + *n*-nonanol (C_{60} + *n*-$C_9H_{19}OH$)	−	1	TG	13
C_{60} + *n*-decanol (C_{60} + *n*-$C_{10}H_{21}OH$)	−	1	TG	13
C_{60} + *n*-undecanol (C_{60} + *n*-$C_{11}H_{23}OH$)	−	1	TG	13
C_{60} + natural oils, animal fats		0.17 ± 0.05	TG	30
		Solid Solvates of C_{70}		
C_{70} + 1,2-dimethylbenzene	283.0 ± 1.2	3.0 to 4.0	TG	48
(C_{70} + 1,2-$C_6H_4(CH_3)_2$)	368.7 ± 0.8	2.0 ± 0.5		
C_{70} + 1,2-dichlorobenzene	327.9 ± 1.1	−	−	48
(C_{70} + 1,2-$C_6H_4Cl_2$)	397.5 ± 1.0			
C_{70} + bromobenzene (C_{70} + C_6H_5Br)	290 ± 1.0	1.9 ± 0.2	TG	48
C_{70} + 1,3,5-trimethylbenzene (C_{70} + 1,3,5-$C_6H_3(CH_3)_3$)	422.0 ± 2.2	2.0 ± 0.2	DSC	44
C_{70} + butyric acid (C_{70} + C_3H_7COOH)	−	1	TG	51
C_{70} + valeric acid (C_{70} + C_4H_9COOH)	−	1	TG	51
C_{70} + caproic acid (C_{70} + $C_5H_{11}COOH$)	−	1	TG	51
C_{70} + heptanoic acid (C_{70} + $C_6H_{13}COOH$)	−	1	TG	51
C_{70} + caprylic acid (C_{70} + $C_7H_{15}COOH$)	−	1	TG	51
C_{60} + pelargonic acid (C_{70} + $C_8H_{17}COOH$)	−	1	TG	51
C_{70} + natural oils, animal fats		0.17 ± 0.05	TG	30

[a] T_{imp} is the temperature of incongruent melting of the solvate. [b] TG, thermogravimetric method; DSC, differential scanning calorimetry. [c] ±, uncertainty of solvate composition determination.

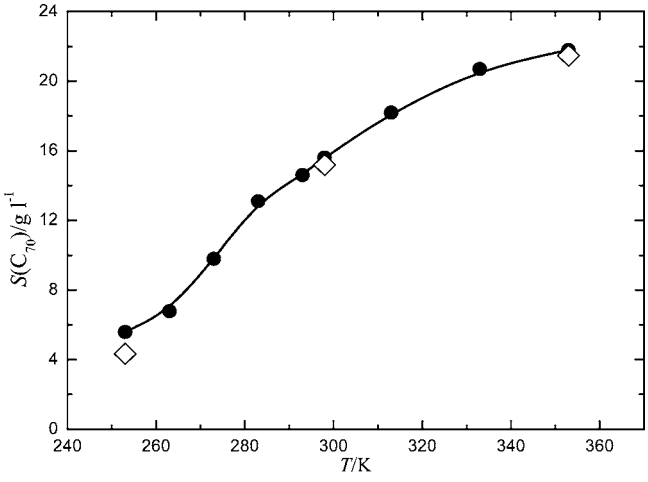

Figure 11. Solubility of the C_{70} fullerene in 1,2-dimethylbenzene. ●, 18; ◇, 89.

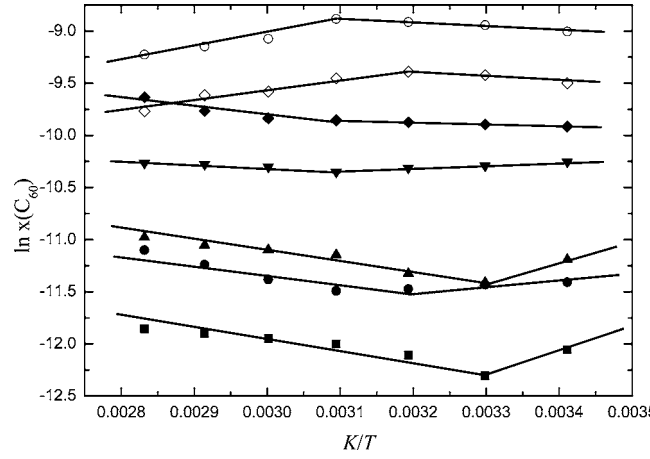

Figure 12. Dependence of logarithm of composition of the C_{60} fullerene in the saturated solution vs inversed temperature in homologous series of alkan-1-ols $C_nH_{2n+1}OH$ (n = 5 to 11). ■, pentan-1-ol; ●, hexan-1-ol, ▲, heptan-1-ol, ▼, octan-1-ol, ♦, nonan-1-ol, ◇, decan-1-ol, ○, undecan-1-ol.

298, and 353) K (see Figures 14 and 15). It was determined that at all temperatures in the two substitutional solid solutions $(C_{60})_x(C_{70})_{1-x}$·*n*(*o*-$C_6H_4(CH_3)_2$) are crystallized, and at 353 K both solid solutions are unsolvated. At 298 K, the solid solution enriched with the C_{60} fullerene is bisolvated, whereas the solid solution enriched with the C_{70} fullerene is unsolvated. At 253 K, both solid solutions are bisolvated (see Table 9). Also, the presence of a eutonic point corresponding to simultaneous saturation with the two solid solutions was determined. The phase diagram of the system enabled the authors to develop a prechromatographic separation of an industrial fullerene mixture. Stukalin et al.[19] investigated the same system (C_{60} + C_{70} + *o*-xylene) and determined the presence of three solid phases and two eutonic points (invariant points, corresponding to simultaneous saturation with two solid phases) in the phase diagram which form two three-phases areas: solid solution based on C_{60}·2(o-$C_6H_4(CH_3)_2$) + eutonic (1) + phase of constant composition $(C_{60})_{0.22}(C_{70})_{0.78}$·4(o-$C_6H_4(CH_3)_2$) and $(C_{60})_{0.22}(C_{70})_{0.78}$·4(*o*-$C_6H_4(CH_3)_2$) + eutonic (2) + C_{70}·2(*o*-$C_6H_4(CH_3)_2$) at 298 K; C_{60} + eutonic (1) + phase of constant composition $(C_{60})_{0.22}(C_{70})_{0.78}$·4(*o*-$C_6H_4(CH_3)_2$) and $(C_{60})_{0.22}(C_{70})_{0.78}$·4(*o*-$C_6H_4(CH_3)_2$) + eutonic (2) + C_{70}·2(*o*-$C_6H_4(CH_3)_2$) at 330 K; C_{60} + eutonic (1) + phase of constant composition $(C_{60})_{0.22}(C_{70})_{0.78}$·*n*(*o*-$C_6H_4(CH_3)_2$), where n < 4 and $(C_{60})_{0.22}(C_{70})_{0.78}$·*n*(*o*-$C_6H_4(CH_3)_2$) + eutonic (2) + C_{70}·2(*o*-$C_6H_4(CH_3)_2$) at 360 K; C_{60} + eutonic (1) + phase of constant composition $(C_{60})_{0.22}(C_{70})_{0.78}$·*n*(*o*-$C_6H_4(CH_3)_2$), where n < 4 and $(C_{60})_{0.22}(C_{70})_{0.78}$·*n*(*o*-$C_6H_4(CH_3)_2$) + eutonic (2) + C_{70} at 380 K.

We have previously studied the ternary system C_{60} + C_{70} + styrene at (258, 273, and 298) K (see Table 9).[26,27] We chose this ternary systems for the following reasons. It is known that

Table 8. Solubility of the C_{60} Fullerene in the Binary Systems (a) C_{60} + Toluene ($C_6H_5CH_3$) as a Function of Temperature and Pressure[38] and (b) C_{60} + Hexane (C_6H_{14}) at 298.2 K[80]

(a)		*T*/K		
P/MPa	278.2	288.2	298.2	308.2
		S/g·L^{-1}		
0.1	5.30	4.65	4.13	3.73
21	n.d.[a]	6.57	n.d.[a]	n.d.[a]
43	n.d.[a]	10.3	8.86	7.35
77	n.d.[a]	7.41	n.d.[a]	n.d.[a]
85	4.57	7.19	10.5	11.6
102	n.d.[a]	n.d.[a]	9.23	n.d.[a]
111	n.d.[a]	6.41	n.d.[a]	12.59
128	3.96	5.84	7.95	11.47
145	n.d.[a]	n.d.[a]	7.42	10.71
170	3.17	4.67	6.81	9.53
213	2.77	4.09	5.67	7.23
255	2.41	3.13	4.67	6.08
298	2.15	2.79	4.19	4.94
340	2.01	2.52	3.54	4.11

(b)	
P/MPa	S/g·L^{-1}
50	0.102
100	0.165
150	0.213
200	0.230
250	0.256
300	0.281
350	0.290
400	0.324

[a] n.d - not determined.

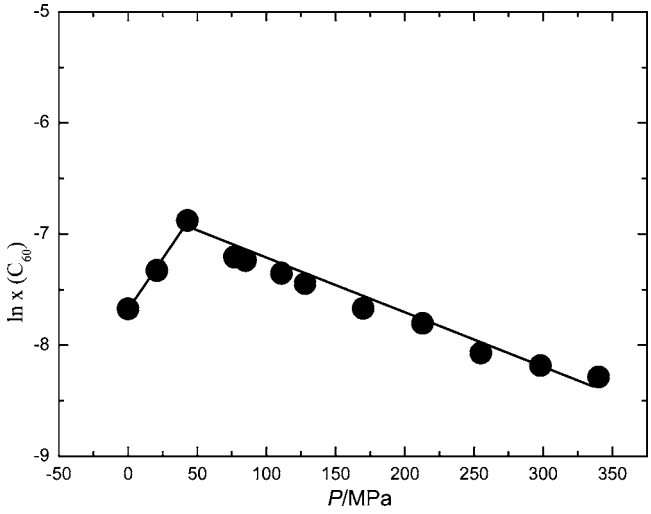

Figure 13. Dependence of logarithm of mole fraction x of the C_{60} fullerene in the saturated solution vs pressure in the C_{60}−toluene system at $T = 288.2$ K.

an admixture of both fullerenes and the fullerene mixture to a liquid/melt monomer, followed by polymerization, can form a fullerene-containing copolymer, if the formation of true solution/melt occurs. New polymer materials with unique or at least with improved commercial characteristics can be prepared this way. Styrene is one of a few monomers, capable of copolymerization and at the same time allowing to reach a high true solubility of light fullerenes of up to 10 g·L^{-1}.

The solubility diagrams of the ternary system C_{60} + C_{70} + $C_6H_5CH{=}CH_2$ at (258, 273, and 298) K consist of two branches. The first one corresponds to crystallization of bisolvated solid solutions $(C_{60})_x(C_{70})_{1-x}$·$2C_6H_5CH{=}CH_2$ enriched with the C_{60} fullerene, while the second one corresponds to crystallization

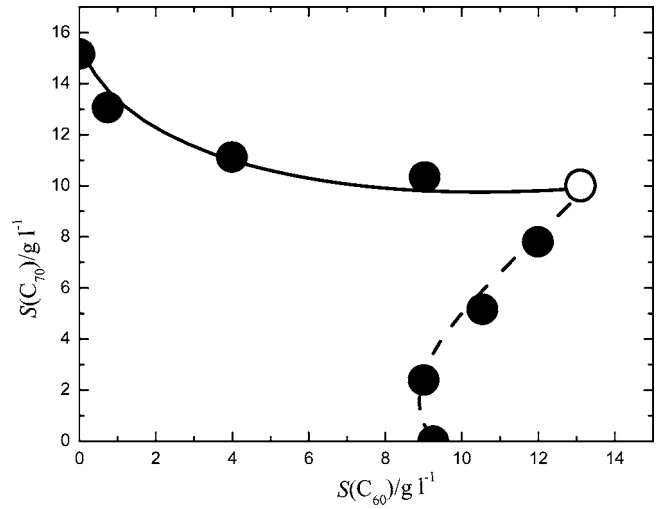

Figure 14. Solubility diagram in the ternary system C_{60} + C_{70} + 1,2-dimethylbenzene (*o*-$C_6H_4(CH_3)_2$) at $T = 298$ K. Solid line corresponds to crystallization of $(C_{60})_x(C_{70})_{1-x}$; dashed line corresponds to crystallization of $(C_{60})_x(C_{70})_{1-x}$·$2C_6H_5(CH_3)_2$. $S(C_{60})$, concentration of C_{60} in solution; $S(C_{70})$, concentration of C_{70} in solution. "○" corresponds to simultaneous saturation of two solids.

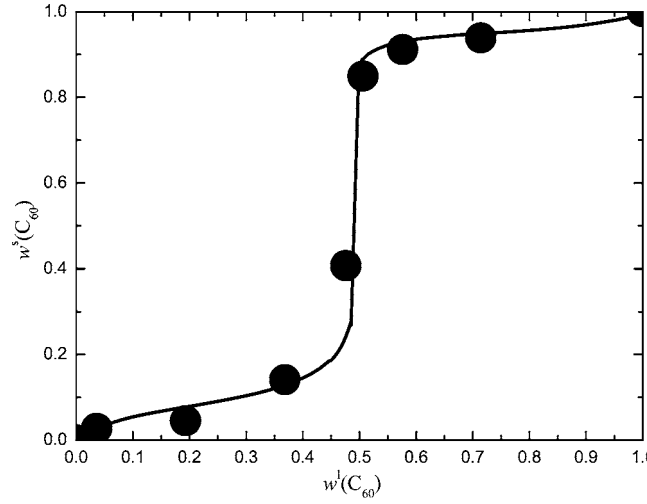

Figure 15. Fullerene component distribution between liquid and solid solutions in the ternary system C_{60} + C_{70} + 1,2-dimethylbenzene ($C_6H_4(CH_3)_2$) at $T = 298$ K. $w^l(C_{60})$ is the mass fraction of the C_{60} fullerene in the liquid solution, and $w^s(C_{60})$ is the mass fraction of the C_{60} fullerene in solid solution.

of the unsolvated solid solutions $(C_{60})_x(C_{70})_{1-x}$, enriched with the C_{70} fullerene. At any temperature, there is the only invariant point corresponding to simultaneous saturation with the two solid solutions.[93−95] During crystallization, the immiscibility 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. A salting-in effect is observed in the crystallization branches of the bisolvated solid solutions enriched with the C_{60} fullerene; i.e., the concentration of C_{60} increases with the concentration of C_{70} in saturated solutions. However, in the crystallization branches of unsolvated solid solutions enriched with the C_{70} fullerene, the salting-out effect is observed; i.e., the concentration of the C_{70} fullerene decreases monotonously with increase of the C_{60} fullerene concentration (see Figures 16 and 17). Noteworthy is that the investigation of phase equilibrium in this system can help to optimize the thermocatalytic process of synthesis of polystyrene modified with fullerenes.

We have previously studied the solubility of an industrial fullerene mixture (60 % of C_{60} + 39 % of C_{70} + 1 % of

Table 9. Equilibrium Liquid−Solid Phase Composition in the Ternary Systems: $C_{60}^{(1)} + C_{70}^{(2)} + 1,2\text{-}C_6H_4(CH_3)_2^{(3)}$ at (253.15, 298.15, and 353.15) K; $C_{60} + C_{70} + C_6H_5CH{=}CH_2$ at (258.15, 273.15, and 298.15) K[a,b]

$S(C_{60})$ / g·L^{-1}	$S(C_{70})$ / g·L^{-1}	$w^l(C_{60})$ / %	$w^s(C_{60})$ / %	solid phase
		$C_{60} + C_{70}$ + 1,2-Dimethylbenzene (1,2-$C_6H_4(CH_3)_2$)50, 96		
			$T = 353.15$ K	
4.44	0.00	1.00	1.00	C_{60}
3.78	2.06	0.647	0.950	$(C_{60})_x(C_{70})_{1-x}$ (2)
4.15	4.26	0.493	0.900	$(C_{60})_x(C_{70})_{1-x}$ (2)
5.26	7.50	0.412	0.850	$(C_{60})_x(C_{70})_{1-x}$ (2)
6.74	11.18	0.376	0.327	$(C_{60})_x(C_{70})_{1-x}$ (1)+ $(C_{60})_x(C_{70})_{1-x}$ (2)
4.59	11.18	0.291	0.120	$(C_{60})_x(C_{70})_{1-x}$ (1)
2.15	13.23	0.140	0.045	$(C_{60})_x(C_{70})_{1-x}$ (1)
0.55	16.76	0.032	0.027	$(C_{60})_x(C_{70})_{1-x}$ (1)
0.00	21.47	0.000	0.000	C_{70}
			$T = 298.15$ K	
9.25	0.00	1.00	1.00	$C_{60}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$
9.00	2.40	0.714	0.939	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (2)
10.54	5.17	0.576	0.912	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4\ (CH_3)_2)$ (2)
11.99	7.80	0.506	0.850	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4\ (CH_3)_2)$ (2)
13.11	9.98	0.476	0.407	$(C_{60})_x(C_{70})_{1-x}$ (1) + $(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4\ (CH_3)_2)$ (2)
9.03	10.34	0.368	0.141	$(C_{60})_x(C_{70})_{1-x}$ (1)
3.99	11.12	0.193	0.045	$(C_{60})_x(C_{70})_{1-x}$ (1)
0.74	13.07	0.036	0.027	$(C_{60})_x(C_{70})_{1-x}$ (1)
0.00	15.17	0.000	0.000	C_{70} (1)
			$T = 253.15$ K	
0.00	4.34	0.000	0.000	$C_{70}\cdot 2(o\text{-}C_6H_4\ (CH_3)_2)$
0.95	3.20	0.230	0.048	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (1)
2.39	2.90	0.452	0.110	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (1)
2.16	4.20	0.509	0.402	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (1) + $(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (2)
3.43	1.75	0.653	0.897	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (2)
2.33	0.77	0.751	0.951	$(C_{60})_x(C_{70})_{1-x}\cdot 2(o\text{-}C_6H_4(CH_3)_2)$ (2)
1.81	0.00	1.000	1.000	$C_{60}\cdot 2(o\text{-}C_6H_4\ (CH_3)_2)$
		$C_{60} + C_{70} + C_6H_5CH{=}CH_2$26, 27, 69		
			$T = 298.15$ K	
4.02	0.00	1.00	1.00	$C_{60}\cdot 2C_6H_5CH{=}CH_2$
4.88	0.11	0.98	0.93	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
5.64	0.32	0.95	0.89	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
6.55	0.77	0.90	0.83	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
6.96	1.08	0.87	0.80	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.20	1.70	0.80	0.75	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.84	2.63	0.75	0.70	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
8.46	3.08	0.73	0.67	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
8.55	4.00	0.64	0.59	$(C_{60})_x(C_{70})_{1-x}$ (2) + $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
6.03	3.99	0.60	0.50	$(C_{60})_x(C_{70})_{1-x}$ (2)
4.97	4.02	0.55	0.40	$(C_{60})_x(C_{70})_{1-x}$ (2)
2.61	4.30	0.39	0.30	$(C_{60})_x(C_{70})_{1-x}$ (2)
2.07	4.85	0.30	0.20	$(C_{60})_x(C_{70})_{1-x}$ (2)
1.27	5.25	0.19	0.15	$(C_{60})_x(C_{70})_{1-x}$ (2)
0.60	6.02	0.09	0.05	$(C_{60})_x(C_{70})_{1-x}$ (2)
0.00	6.02	0.00	0.00	C_{70}
			$T = 273.15$ K	
5.50	0.00	1.00	1.00	$C_{60}\cdot 2C_6H_5CH{=}CH_2$
6.84	1.29	0.84	0.89	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.22	2.17	0.77	0.86	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.24	2.39	0.76	0.81	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.69	3.57	0.76	0.74	$(C_{60})_x(C_{70})_{1-x}$ (2) + $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
5.45	3.79	0.59	0.50	$(C_{60})_x(C_{70})_{1-x}$ (2)
4.99	4.20	0.54	0.38	$(C_{60})_x(C_{70})_{1-x}$ (2)
3.84	4.59	0.46	0.32	$(C_{60})_x(C_{70})_{1-x}$ (2)
2.53	5.38	0.32	0.23	$(C_{60})_x(C_{70})_{1-x}$ (2)
0	5.60	0.00	0.00	C_{70}
			$T = 258.15$ K	
5.90	0.00	1.00	1.00	$C_{60}\cdot 2C_6H_5CH{=}CH_2$
6.41	0.49	0.93	0.86	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.16	1.23	0.85	0.84	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
7.84	2.62	0.75	0.71	$(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
8.01	3.56	0.69	0.66	$(C_{60})_x(C_{70})_{1-x}$ (2) + $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$ (1)
5.33	2.69	0.66	0.46	$(C_{60})_x(C_{70})_{1-x}$ (2)
2.97	2.75	0.52	0.37	$(C_{60})_x(C_{70})_{1-x}$ (2)
2.01	2.78	0.42	0.26	$(C_{60})_x(C_{70})_{1-x}$ (2)
1.35	2.80	0.33	0.17	$(C_{60})_x(C_{70})_{1-x}$ (2)
0.31	2.82	0.1	0.09	$(C_{60})_x(C_{70})_{1\text{-}x}$ (2)
0.00	2.84	0.00	0.00	C_{70}

[a] (1), (2)-solid solutions enriched by C_{60} and C_{70} fullerenes correspondingly. [b] $S(C_{60})$, concentration of C_{60} in solution; $S(C_{70})$, 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.[26,27,50,69,96]

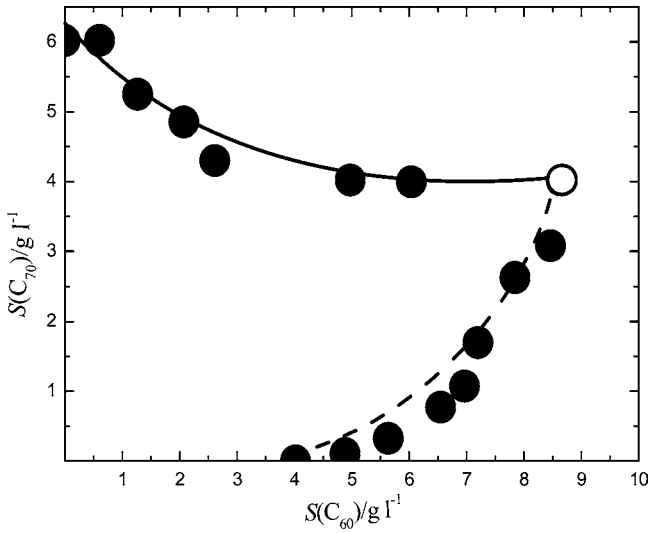

Figure 16. Solubility diagram in the ternary system $C_{60} + C_{70}$ + styrene ($C_6H_5CH{=}CH_2$) at $T = 298$ K. Solid line corresponds to crystallization of $(C_{60})_x(C_{70})_{1-x}$; dashed line corresponds to crystallization of $(C_{60})_x(C_{70})_{1-x}\cdot 2C_6H_5CH{=}CH_2$. $S(C_{60})$, concentration of C_{60} in solution; $S(C_{70})$, concentration of C_{70} in solution. "○" corresponds to simultaneous saturation of two solids.

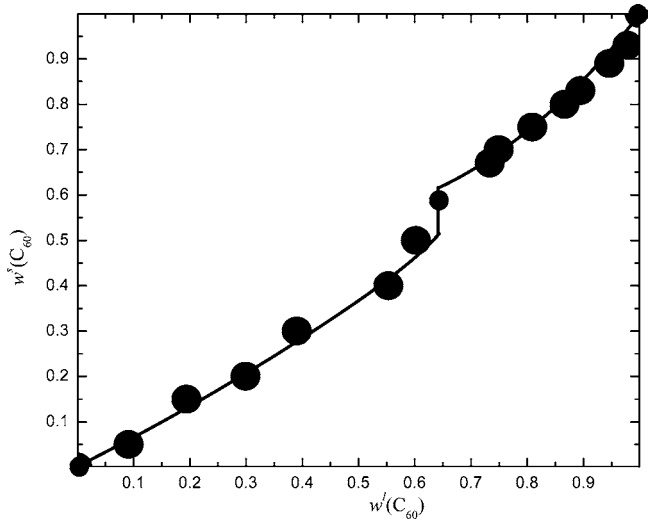

Figure 17. Fullerene component distribution between liquid and solid solutions in the ternary system $C_{60} + C_{70} + C_6H_5CH{=}CH_2$ at $T = 298$ K. $w^l(C_{60})$ is the mass fraction of the C_{60} fullerene in liquid solution; $w^s(C_{60})$ is the mass fraction of the C_{60} fullerene in solid solution.

$C_{76}-C_{90}$) in different solvents (1-alcohols, carboxylic acids, heptane, and styrene) in the temperature range $T = (293$ to $353)$ K (see Table 10).[6,13,16,57−59] It is significant that such investigations are useful for developing chromatographic and prechromatographic (based on liquid−liquid and liquid−solid equilibria) methods of light fullerenes separation.

C_{60} Solvent (1)−Solvent (2). Data on the solubility of an individual light fullerene in mixed solvents are limited. The solubility of fullerenes has been investigated in ten systems, while the temperature dependence has been investigated in two systems. Such studies are important because a knowledge of the fullerene solvation mechanism can allow one to selectively carry out chemical reactions with participation of fullerenes as well as to develop effective criteria for selection of solvents for separation of fullerene mixtures.

Kolker et al.[42,43] studied the C_{60} fullerene solubility in tetrachloromethane + toluene and tetrachloromethane + *o*-dichlorobenzene mixtures in the temperature range $T = (298.15$ to $338.15)$ K (see Table 11). In this work, the equations

Table 10. Temperature Dependences of Solubility of the Industrial Fullerene Mixture Solubility with Mass Fraction (60 to 65) % of C_{60} + (33 to 39) % of C_{70} + (1 to 2) % of $C_{76}-C_{90}$)* in Various Solvents[6,13,16,57−59]

	T/K							
solvent	293.15	303.15	313.15	323.15	333.15	343.15	353.15	ref
	S/g·L^{-1}							
butyric acid	0.032[a]; 0.016[b]	0.038[a]; 0.018[b]	0.052[a]; 0.031[b]	0.053[a]; 0.037[b]	0.055[a]; 0.053[b]	0.064[a]; 0.075[b]	0.067[a] 0.085[b]	57
valeric acid	0.194[a]; 0.039[b]	0.190[a]; 0.041[b]	0.148[a]; 0.046[b]	0.135[a]; 0.048[b]	0.147[a]; 0.047[b]	0.159[a]; 0.054[b]	0.162[a]; 0.071[b]	58
caproic acid	0.424[a]; 0.303[b]	0.405[a]; 0.290[b]	0.344[a]; 0.275[b]	0.315[a]; 0.263[b]	0.310[a]; 0.258[b]	0.241[a]; 0.254[b]	0.258[a]; 0.315[b]	58
heptanoic acid	0.491[a]; 0.374[b]	0.472[a]; 0.374[b]	0.456[a]; 0.375[b]	0.421[a]; 0.376[b]	0.464[a]; 0.434[b]	0.417[a]; 0.429[b]	0.334[a]; 0.512[b]	57
caprylic acid	0.183[a]; 0.144[b]	0.190[a]; 0.144[b]	0.176[a]; 0.181[b]	0.188[a]; 0.218[b]	0.246[a]; 0.217[b]	0.269[a]; 0.216[b]	0.308[a]; 0.230[b]	59
pelargonic acid	0.598[a]; 0.182[b]	0.615[a]; 0.238[b]	0.675[a]; 0.237[b]	0.715[a]; 0.237[b]	0.575[a]; 0.240[b]	0.537[a]; 0.273[b]	0.541[a]; 0.337[b]	59
n-pentanol-1	0.071[a]; 0.040[b]	0.054[a]; 0.040[b]	0.062[a]; 0.039[b]	0.069[a]; 0.039[b]	0.079[a]; 0.054[b]	0.090[a]; 0.079[b]	0.099[a]; 0.079[b]	13
n-hexanol-1	0.140[a]; 0.172[b]	0.130[a]; 0.156[b]	0.128[a]; 0.124[b]	0.118[a]; 0.125[b]	0.138[a]; 0.124[b]	0.145[a]; 0.114[b]	0.157[a]; 0.108[b]	13
n-heptanol-1	0.078[a]; 0.042[b]	0.071[a]; 0.042[b]	0.079[a]; 0.052[b]	0.080[a]; 0.064[b]	0.093[a]; 0.064[b]	0.100[a]; 0.063[b]	0.114[a]; 0.063[b]	13
n-octanol-1	0.248[a]; 0.087[b]	0.230[a]; 0.088[b]	0.219[a]; 0.088[b]	0.214[a]; 0.088[b]	0.227[a]; 0.101[b]	0.233[a]; 0.114[b]	0.243[a]; 0.154[b]	13
n-nonanol-1	0.437[a]; 0.196[b]	0.402[a]; 0.197[b]	0.356[a]; 0.217[b]	0.353[a]; 0.217[b]	0.350[a]; 0.217[b]	0.350[a]; 0.224[b]	0.348[a]; 0.258[b]	13
n-decanol-1	0.576[a]; 0.282[b]	0.617[a]; 0.352[b]	0.629[a]; 0.352[b]	0.582[a]; 0.353[b]	0.559[a]; 0.354[b]	0.536[a]; 0.354[b]	0.424[a]; 0.433[b]	13
n-undecanol-1	0.507[a]; 0.434[b]	0.615[a]; 0.416[b]	0.620[a]; 0.399[b]	0.664[a]; 0.398[b]	0.624[a]; 0.399[b]	0.585[a]; 0.400[b]	0.561[a]; 0.337[b]	13
styrene	6.600[a]; 2.760[b]	7.651[a]; 3.320[b]	9.450[a]; 4.172[b]	7.800[a]; 3.780[b]	5.700[a]; 3.520[b]	3.967[a]; 2.830[b]	2.979[a]; 2.498[b]	25, 27

[a] Corresponds to solubility of C_{60} from fullerene mixture. [b] Corresponds to solubility of C_{70} from fullerene mixture.

Table 11. Temperature Dependences of Mole Fraction Solubility x of the C_{60} Fullerene (3) in Tetrachloromethane (1) + Toluene (2) and Tetrachloromethane (1) + *o*-Dichlorobenzene (2)[42,43]

	T/K				
w_2	298.15	308.15	318.15	328.15	338.15
	Tetrachloromethane (1) + Toluene (2)				
	10^4x_3				
0	0.376	0.423	0.401	0.407	0.413
0.103	0.503	0.510	0.517	0.525	0.532
0.302	0.680	0.831	0.828	0.839	0.793
0.502	1.18	1.25	1.22	1.33	1.33
0.706	1.82	1.77	1.83	1.97	1.75
0.890	2.83	3.07	2.56	2.44	2.32
1	3.61	3.31	3.12	3.00	2.80
	Tetrachloromethane (1) + *o*-Dichlorobenzene (2)				
	10^4x_3				
0	0.376	0.423	0.401	0.406	0.413
0.103	0.63	0.693	0.632	0.655	0.692
0.306	1.7	1.8	1.7	1.91	2.15
0.500	4.52	4.72	4.77	5.13	5.34
0.691	9.94	11.7	12.0	12.1	11.1
0.900	29.3	31.1	18.8	16.0	17.8
1	42.2	36.3	23.4	19.1	21.9

Table 12. Solubility of the C_{60} Fullerene in Decalin (1) + Naphthalene (2), Toluene (1) + Naphthalene (2), and Dodecane (1) + Naphthalene (2) Solvent Mixtures[36]

decalin (1) + naphthalene (2)		toluene (1) + naphthalene (2)		dodecane (1) + naphthalene (2)	
100 w_2	S/g·L^{-1}	100 w_2	S/g·L^{-1}	100 w_2	S/g·L^{-1}
0	1.7	0	2.7	0	0.09
5	2.0	10	3.8	2.5	0.07
10	2.4	15	4.5	5	0.1
15	3.5	20	7.2	6	0.11
		25	7.0	7.8	0.11
		30	7.0	10	0.15
				10.1	0.23

Table 13. Solubility of the C_{60} Fullerene in Acetonitrile (1) + Toluene (2) Solvent Mixtures[87]

100 w_2	S/g·L^{-1}	100 w_2	S/g·L^{-1}
0	0.000	60	0.067
5	0.003	80	0.300
10	0.005	90	0.710
30	0.018	95	0.920
50	0.031	100	2.600

describing the solubility dependence on temperature and solvent composition were derived, and thermodynamic functions of the C_{60} solution were calculated. The temperatures and enthalpies of incongruent melting of the solid solvates were determined using DSC.

Beck[36,87] investigated the isothermal solubility of the C_{60} fullerene in decaline + naphthalene, toluene + naphthalene, dodecane + naphthalene, and acetonitrile + toluene. Their experimental data listed in this paper are summarized in Tables 12 and 13.[36,87]

Kulkarni et al.[14,97] measured isothermal solubility of C_{60} in toluene + acetonitrile, toluene + ethanol, toluene + tetrahydrofuran, acetonitrile + tetrahydrofuran, ethanol + water, and tetrahydrofuran + water (see Table 14) solvent mixtures, and the solubility data were modeled using the Wohl equation.

Solubility of Light Fullerenes in Multicomponent Systems. Studies on the solubility of light fullerenes in natural solvents (vegetable oils, animal, fats and essential oils) are extremely important for the following reasons:

Fullerenes are soluble in natural solvents with the solubility varing from (0.1 to 1) g·L^{-1} tenth to units gram of fullerenes per liter of solvent;

Table 14. Solubility of the C_{60} Fullerene in Toluene (1) + Acetonitrile (2), Toluene (1) + Ethanol (2), Toluene (1) + Tetrahydrofuran (2), Acetonitrile (1) + Tetrahydrofuran (2), Ethanol (1) + Water (2), and Tetrahydrofuran (1) + Water (2)[a]

ethanol (1) + water (2)		tetrahydrofuran (1) + water (2)		toluene (1) + acetonitrile (2)	
$Ø_1$	S/g·L^{-1}	$Ø_1$	S/g·L^{-1}	$Ø_1$	S/g·L^{-1}
0	$8.00\cdot10^{-9}$	0	$8.00\cdot10^{-9}$	0	$4.37\cdot10^{-5}$
					$5.16\cdot10^{-5}$
					$4.24\cdot10^{-5}$
					$4.61\cdot10^{-5}$
0.5	$1.18\cdot10^{-6}$	0.5	$1.23\cdot10^{-5}$	0.3	$2.39\cdot10^{-3}$
	$1.45\cdot10^{-6}$		$2.73\cdot10^{-5}$		$2.41\cdot10^{-3}$
0.6	$4.96\cdot10^{-6}$	0.6	$8.98\cdot10^{-5}$	0.5	0.0222
	$4.97\cdot10^{-6}$		$9.36\cdot10^{-5}$		0.0215
0.7	$2.89\cdot10^{-5}$	0.7	$3.15\cdot10^{-4}$	0.7	0.244
	$2.41\cdot10^{-5}$		$3.18\cdot10^{-4}$		0.284
0.8	$7.07\cdot10^{-5}$	0.8	$1.02\cdot10^{-3}$	0.9	1.11
	$7.32\cdot10^{-5}$				1.09
0.9	$4.51\cdot10^{-4}$	0.9	$3.06\cdot10^{-3}$	1	3.09
	$4.41\cdot10^{-4}$		$3.32\cdot10^{-3}$		2.96
1	$1.74\cdot10^{-3}$	1	$1.14\cdot10^{-2}$		
	$1.43\cdot10^{-3}$		$1.08\cdot10^{-2}$		

toluene (1) + ethanol (2)		tetrahydrofuran (1) + acetonitrile (2)		tetrahydrofuran (1) + toluene (2)	
$Ø_1$	S/g·L^{-1}	$Ø_1$	S/g·L^{-1}	$Ø_1$	S/g·L^{-1}
0	$2.00\cdot10^{-3}$	0	$4.70\cdot10^{-5}$	0	0.0116
			$4.30\cdot10^{-5}$		0.0111
			$3.70\cdot10^{-5}$		
0.1	$2.79\cdot10^{-3}$	0.1	$1.10\cdot10^{-4}$	0.05	0.0111
	$3.04\cdot10^{-3}$		$9.40\cdot10^{-5}$		0.0106
0.3	0.0237	0.15	$4.70\cdot10^{-5}$	0.1	0.0145
	0.0232				0.0141
0.5	0.124	0.2	$6.60\cdot10^{-5}$	0.15	0.0138
	0.121		$4.90\cdot10^{-5}$		0.0136
0.7	0.494	0.25	$6.70\cdot10^{-5}$	0.2	0.0174
	0.542				0.0166
0.9	1.38	0.4	$1.60\cdot10^{-4}$	0.3	0.0217
	1.38		$1.20\cdot10^{-4}$		0.0144
1	3.00	0.5	$2.80\cdot10^{-4}$	0.35	0.0245
					0.0241
		0.6	$5.70\cdot10^{-4}$	0.50	0.0458
			$6.10\cdot10^{-4}$		0.0463
		0.75	$1.59\cdot10^{-3}$	0.6	0.0660
			$1.61\cdot10^{-3}$		0.0641
		0.8	$2.57\cdot10^{-3}$	0.65	0.0890
			$3.08\cdot10^{-3}$		0.0957
		0.9	$5.59\cdot10^{-3}$	0.7	0.104
			$6.40\cdot10^{-3}$		0.130
		1	0.0111	0.75	0.180
			0.0105		0.160
				0.8	0.323
					0.284
				0.9	1.23
					1.18
				1	3.09
					2.96

[a] $Ø_1$, volume fraction of component 1.[14,97] The values of solubility are absent in ref 14. The authors kindly shared with us these values. The rounding of the values of solubility down to 3 digits after comma was performed by us.

Table 15. Solubility of Light Fullerenes in Natural Oils (Temperatures Different From 298 K Are Presented in Brackets)

	T/K					
solvent	273.15	293.15	313.15	333.15	353.15	ref
		$S(C_{60})/g \cdot L^{-1}$				
≪Stavropolje≫ (unrefined sunflower oil)	0.294	0.451	0.727	0.708	0.638	29
≪Zlato≫ (refined sunflower oil)	0.299	0.377	0.456	0.570	0.697	29
sunflower triglyceride		0.116				33
sunflower oil ≪Venus≫		6.91				31
sunflower oil ≪Floriol≫		4.01				31
sunflower oil ≪Eden≫		5.62				31
≪Milora≫ (corn oil)	0.196	0.609	0.846	0.945	1.319	29
walnut oil	0.269	0.485	0.694	0.718	1.017	29
	0.264	0.470	0.751	0.858	1.206	29
olive oil	5.99 (283.15 K)	4.61 (303 K)	3.88 (313 K)			31
		0.909				32
			23.6[a] (323 K)			47
olive oil ≪Carapelli≫		2.84				31
olive oil ≪Borgess≫		5.97				31
olive oil ≪Olatalia≫		3.97				31
olive triglyceride		0.173				33
	0.229	0.513	0.639	0.717	1.033	29
linseed oil		0.365				32
				53.1[a] (328 K)		47
linseed triglyceride		0.091				33
pignolia oil	0.323	0.485	0.818	1.053	1.099	29
grape-seed oil	0.327	0.371	0.663	0.748	0.897	29
apricot-kernel oil	0.372	0.509	0.702	0.799	0.958	29
brassica methyl ester (biodiesel)		0.187				33
		0.859				32
soybean triglyceride		0.134				33
castor oil		0.392				32
peanut oil		0.751				32
sunseed oil		0.522				32
soybean oil		0.495				32
sea-buckthorn				43.2[a](328 K)		47
cedur oil				51.8[a](343 K)		47
		$S(C_{70})/g \cdot L^{-1}$				
≪Stavropolje≫ (unrefined sunflower oil)	0.504	1.827	2.647	2.872	3.213	30
≪Zlato≫ (refined sunflower oil)	0.303	1.289	1.668	2.996	3.261	30
≪Milora≫ (corn oil)	0.506	1.957	2.963	3.404	4.286	30
walnut oil	0.315	1.390	1.829	2.650	2.837	30
olive oil	0.402	0.756	1.286	2.735	3.278	30
		1.035				32
linseed oil	0.505	1.198	1.639	2.118	2.773	30
		0.727				32
pignolia oil	0.378	0.757	1.512	2.020	2.710	30
grape-seed oil	0.632	0.947	1.578	2.207	2.838	30
apricot-kernel oil	0.378	1.009	2.208	2.772	3.090	30
castor oil		0.636				32
peanut oil		0.852				32
sunseed oil		0.867				32
soybean oil		0.753				32
brassica oil		1.034				32
		S(60 % to 65 % C_{60} + 33 % to 39 % C_{70} + 1 % to 2 % C_{76-90} mass fraction)/$g \cdot L^{-1}$ [b]				
≪Stavropolje≫ (unrefined sunflower oil)	1.831	2.234	2.068	1.839	1.612	29
	0.898	1.045	1.361	1.843	2.320	29
≪Zlato≫ (refined sunflower oil)	1.828	2.284	2.510	2.663	2.864	29
	1.279	1.456	1.731	1.825	2.199	29
≪Milora≫ (corn oil)	1.949	2.294	2.746	2.619	2.735	29
	1.209	1.201	1.346	1.664	1.976	29
walnut oil	1.378	2.127	2.156	2.264	2.340	29
	0.752	0.890	1.362	1.517	1.546	29
olive oil	1.239	2.900	2.224	2.135	2.150	29
	0.913	1.123	1.518	1.747	1.999	29
linseed oil	1.733	2.097	2.067	1.987	1.923	29
	0.900	1.117	1.207	1.524	1.778	29
pignolia oil	1.711	2.026	2.479	2.484	2.607	29
	1.370	1.681[b]	1.826	2.079	2.294	29
grape-seed oil	1.693	1.801	2.092	2.263	2.224	29
	1.059	1.214	1.301	1.517	1.675	29
apricot-kernel oil	1.437	1.791	1.905	2.086	2.097	29
	0.908	1.056	1.463	1.487	1.553	29

[a] Saturation of fullerene solutions was carried out using ultrasonic machining. [b] Upper value corresponds to the solubility of C_{60} from the fullerene mixture; lower value corresponds to the solubility of C_{70} from the fullerene mixture.

Table 16. Solubility of Light Fullerenes in Animal Fats

solvent	*T*/K 323.15 K	333.15 K	343.15 K	353.15 K	ref
		$S(C_{60})/g\cdot L^{-1}$			
pork fat	0.052	0.145	0.231	0.257	34
bird fat	0.024	0.059	0.093	0.122	34
beef fat	0.041	0.131	0.153	0.168	34
margarine ≪Rumjashka≫	–	0.019	0.028	0.029	34
lamb fat	0.041	0.212	0.385	0.541	34
desi	0.021	0.046	0.063	0.087	34
molten cow butter		soluble			32
cod-liver oil		53.0[a] (338 K)			47
		$S(C_{70})/g\cdot L^{-1}$			
pork fat	0.143	0.291	0.529	0.582	34
bird fat	0.148	0.344	0.661	0.688	34
beef fat	0.054	0.096	0.134	0.160	34
margarine ≪Rumjashka≫	–	0.080	0.132	0.252	34
lamb fat	0.053	0.132	0.238	0.317	34
desi	0.159	0.360	0.556	0.587	34
molten cow butter		soluble			32
		S(60 % to 65 % C_{60} + 33 % to 39 % C_{70} + 1 % to 2 % C_{76-90} mass fraction)/g·L^{-1} [b]			
pork fat	0.109 0.184	0.437 0.381	0.649 0.571	0.650 0.670	34
bird fat	0.195 0.191	0.401 0.284	0.533 0.428	0.571 0.495	34
beef fat	0.126 0.045	0.226 0.190	0.521 0.477	0.551 0.476	34
margarine ≪Rumjashka≫	– –	0.021 0.098	0.135 0.193	0.199 0.240	34
lamb fat	0.058 0.194	0.282 0.306	0.409 0.460	0.512 0.546	34
desi	0.177 0.154	0.261 0.258	0.354 0.309	0.426 0.368	34

[a] Saturation of fullerene solutions was carried out using ultrasonic machining. [b] Upper value corresponds to solubility of C_{60} from the fullerene mixture; lower value corresponds to solubility of C_{70} from the fullerene mixture.

Further, fullerene solutions in these natural solvents are stable and absolutely transparent true solutions;

Additionally, these solutions are nontoxic and biocompatible with respect to animals and humans when they are prepared by extraction of a fullerene mixture from fullerene soot by natural oils and adipose; i.e., they do not contain any toxic impurities. Individual fullerenes obtained from solutions in aromatic solvents (toluene, *o*-xylene, dichlorobenzene) well contain residuals of these solvents which are retained even after drying under vacuum at 1.33 Pa and t = (473 to 523) °C, their content varying from (0.001 to 0.01) %. An alternative way for the complete purification of a fullerene from solvent admixtures is a high-temperature sublimation of a fullerene at low pressure (≈0.001 Pa), but the latter process is very expensive and laborious;

Fullerene solutions in oils and fats possess pronounced antibacterial and antioxidative properties, and they can absorb free radicals and ionic radicals from condensed phases in which they are present as well as photons in the ultraviolet area region.[30−34]

Due to the complexity of these solvents, there are no theoretical approaches for prediction of solubility of fullerenes except for the work in which solubility of individual light fullerenes was qualitatively estimated using Hansen's solubility model.[32] All available experimental data on the solubility of fullerenes in liquid natural vegetable oils, animal fats, and essential oils are summarized in Tables 15, 16, and 17.

We have also studied solid solvate formation in systems of individual light fullerenes with natural oils and animal fats.[29,30,34] Because the quantities of di- and monoglycerides, phospholipids, glycolipids, diolic lipids, free fatty acids, stearins and their esters, dye-stuffs, vitamins, polyphenols and their esters, and other substances are present as traces in a given oil, the oils (fats) can be considered to consist entirely of triglycerides. Such an assumption is quite reasonable as the content of triglycerides is actually high and reaches up to 98 % in vegetable oils. For a hypothetic oil consisting of the only triglyceride (for example, of the only triglyceride TG ≡ $R_1(CO)OCH_2 - CH(COOR_2) - CH_2O(CO)R_3$, R_1, R_2, R_3 - radicals of saturated and unsaturated fatty acids with molecular mass 10^{2-3} au having the mixed composition), the solid crystal solvate would have a strictly determined composition and a strictly determined dissociation temperature. The dissociation would occur according to the scheme: $C_{60}\cdot N(TG)_{(solid)} \rightarrow C_{60(solid)} + N(TG)_{(liquid)}$. However, in reality the situation described above is impossible. First, natural oils contain five and more various fatty acids which cannot be "packed" into one triglyceride, and second, molar ratios of acids in such a triglyceride must be either 1:1:1 or 1:2 which is never observed for natural oils.

Natural oil is a multicomponent mixture of different triglycerides: $TG_1 + TG_2 + ... + TG_m$ (m is the number of various triglycerides in the particular oil). All such triglycerides could replace each other in the structure of solid crystal solvate, for example, in solid crystal solvate of the following composition: KS ≡ $C_{60}\cdot(TG_1)_{N1}(TG_2)_{N2}...(TG_{m-1})_{Nm-1}(TG_m)_{N-N1-N2-...-Nm-1}$ (N_1, N_2, ..., N_m are the number of various triglycerides in the mixed solvate formed in fullerene−natural oil system) owing to their structural and chemical similarity. So a thermogravimetric experiment carried out[29,30,34] showed that the average composition of the solid crystal solvate formed in the systems individual light fullerenes + natural oils, animal fats is $C_{60,70}\cdot(0.17 \pm 0.05)$TG. Thus, one acid residual in triglyceride holds two molecules of C_{60}.

The industrial mixture of highly isomeric carboxylic acids (mixture of α,α^1-branched isomeric carboxylic acids with carbon chain including 9 to 11 carbon atoms) was chosen as an

Table 17. Solubility of Light Fullerenes in Essential Oils[35,47]

solvent	T/K 293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K
			$S(C_{60})/g\cdot L^{-1}$				
essential oil of carnation	1.551	1.778	2.168	2.880	3.011	3.275	3.864
essential oil of lemon				18.8[a]			
essential oil of orange				21.3[a] (329 K)			
essential oil of cypress				20.6[a]			
essential oil of eucalyptus gum spirit				23.4[a] (328 K)	25.6[a] (338 K)		
			$S(C_{70})/g\cdot L^{-1}$				
essential oil of carnation	0.906	1.026	1.267	1.715	2.037	2.662	5.619
			$S(65\ \%\ C_{60} + 34\ \%\ C_{70} + 1\ \%\ C_{76-90})/g\cdot L^{-1}$ [b]				
essential oil of carnation	3.554	3.544	3.576	3.622	4.057	4.631	7.095
	1.742	1.962	2.108	2.107	2.448	2.463	2.897
essential oil of cade (wood)	3.068	3.205	3.520	4.441	5.403	5.530	5.677
	3.223	3.586	4.239	5.022	5.731	6.315	6.458
essential oil of cade (leafage)	2.872	2.956	3.506	3.793	4.136	4.337	4.348
	3.196	3.278	3.682	4.094	3.246	2.654	2.402

[a] Saturation of fullerene solutions was carried out using ultrasonic machining. [b] Upper value corresponds to solubility of C_{60} from the fullerene mixture; lower value corresponds to solubility of C_{70} from the fullerene mixture.

Table 18. Solubility of Individual Light Fullerenes and Industrial Fullerene Mixture That Includes High Fullerenes with Mass Fraction of C_{60}, $w = 38.8$ %, C_{70}, $w = 33.0$ %, C_{76-78}, $w = 5.6$ %, C_{84}, $w = 8.6$ %, C_{90}, $w = 2.6$ %, C_{96}, $w = 3.3$ % in Highly Isomeric Carboxylic Acids (Mixture of α,α[1]-Branched Isomeric Carboxylic Acids with Carbon Chain Including 9 to 11 Carbon Atoms)[88]

	T/K 293.15	303.15	313.15	323.15	333.15	343.15	353.15
$S(C_{60})/g\cdot L^{-1}$	0.083	0.127	0.157	0.173	0.177	0.178	0.176
$S(C_{70})/g\cdot L^{-1}$	0.157	0.183	0.190	0.287	0.366	0.369	0.531
$S(38.8\ \%\ C_{60} + 33\ \%\ C_{70} + 5.6\ \%\ C_{76-78} + 8.6\ \%\ C_{84} + 2.6\ \%\ C_{90} + 3.3\ \%\ C_{96})$	0.168	0.183	0.183	0.238	0.254	0.385	0.397

extraction agent for fullerenes.[88] The experimental data obtained are listed in Table 18.

Solubility of Fullerene Derivatives in Various Solvents and Solvent Mixtures. There are many studies devoted to the solubility of fullerenes (especially at room temperature) in water and in general to the problems of solubilizing individual light fullerenes by means of formation of water suspensions, stable colloidal solutions, water-soluble complexes with hydrophilic organic molecules (including polymers), and finally by means of formation of water-soluble derivatives. This kind of research is extremely important for the development of medical and cosmetology products based on fullerenes since fullerenes reveal antibacterial, anticancer, and antiviral activity as well as antioxidant properties. All the biological properties listed above along with the fullerene solubilizing methods are described in monograph by Piotrovskyi et al.[89] and are not discussed here.

Analysis of literature data shows that data on isothermal and polythermal solubility of light fullerene derivatives in various solvents are few in number. Only two papers devoted to this question were found. Tian et al.[22,90,91] investigated the isothermal solubility of the C_{60}−piperazine derivative in 13 solvents (benzene, toluene, *o*-xylene, *p*-xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, chlorobenzene, *o*-dichlorobenzene, *m*-diclorobenzene, 1,2,4-dichlorobenzene, bromobenzene, iodobenzene, dicloromethane) at 293 K (see Table 16). They also described the spectrophotometric method for determination of solubility of this complex in various solvents; in the case of the C_{60} + piperazine derivative in 1,3,5-trimethylbenzene, *m*-dichlorobenzene, and iodobenzene, the authors observed from DSC measurements the formation of solid solvates, whereas in the C_{60} + piperazine + *m*-dichlorobenzene system no solvate formation was detected. The temperatures and enthalpies of first-order transition in the incongruent melting points are also presented.[22,90,91]

It is notable that in general the solubility of C_{60}−piperazine is lower than that of C_{60} except in three aromatic solvents (namely, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, and iodobenzene) and in dichloromethane (see Table 19). It is assumed that the functional group of C_{60}−piperazine increases the total polarity of the molecule.

Table 19. Solubility of the Complex [C_{60} + Piperazine ($C_{60}N(CH_2CH_2)_2N$)] in Different Solvents at 298 K[22,44,90,91]

$S(C_{60}N(CH_2CH_2)_2N)$ solvent	$g\cdot L^{-1}$	$S(C_{60}N(CH_2CH_2)_2N)$ solvent	$g\cdot L^{-1}$
benzene	0.50	chlorobenzene	0.63
toluene	0.17	o-dichlorobenzene	1.79
o-xylene	0.72	m-diclorobenzene	6.03
p-xylene	0.20	1,2,4-trichlorobenzene	4.11
			3.58
1,2,4-trimethylbenzene	3.30	bromobenzene	1.59
1,3,5-trimethylbenzene	7.12	iodobenzene	50.30
		dicloromethane	1.37

We have synthesized the bromine derivatives of C_{60} ($C_{60}Br_n$, $n = 6$, 8, 24) and developed a spectrophotometric method of analysis and studied their solubility in *o*-xylene, *o*-dichlorobenzene, 1-decanol, and heptanoic acid in the temperature range (293 to 353) K[92] (see Table 20). Comparative data on the solubility of C_{60} and $C_{60}Br_n$, $n = 6$, 8, and 24 in *o*-xylene, *o*-dichlorobenzene, *n*-decanol-1, and enanthic acid, in the temperature range (293 to 353) K are presented in Figure 18.

Conclusions

The authors have collected and systematized the data on the solubility of individual light fullerenes in binary systems (individual fullerene + solvent), ternary systems (individual fullerene + solvent (1) + solvent (2), C_{60} + C_{70} + single solvent), and multicomponent systems (individual light fullerenes, industrial fullerene mixture + animal fats and natural oils). The data concerning isothermal and polythermal solubility of fullerene derivatives (fullerene bromides and C_{60}-piperazine

Table 20. Solubility of the Bromine Derivative of C_{60} ($C_{60}Br_n$, n = 6, 8, 24) in Different Solvents[92]

	solvent			
T/K	*o*-xylene	*o*-dichlorobenzene	decan-1-ol	enanthic acid
		$S(C_{60}Br_{24})$/g·L^{-1}		
293.15	0.333	0.184	0.497	0.567
303.15	0.390	0.228	0.592	0.638
313.15	0.450	0.239	0.947	0.709
323.15	0.466	0.255	1.421	0.808
333.15	0.488	0.271	2.013	1.084
343.15	0.640	0.320	2.723	1.417
353.15	0.867	0.412	3.789	2.069
		$S(C_{60}Br_8)$/g·L^{-1}		
293.15	1.180	1.491	0.155	0.177
303.15	1.367	1.988	0.242	0.208
313.15	1.615	2.485	0.404	0.404
323.15	1.739	2.734	0.497	0.482
333.15	2.050	3.293	0.777	0.752
343.15	2.547	3.976	1.118	1.056
353.15	3.976	5.591	2.174	1.771
		$S(C_{60}Br_6)$/g·L^{-1}		
293.15	6.662	11.40	1.063	1.114
303.15	9.096	19.30	1.140	1.166
313.15	9.352	23.10	1.166	1.306
323.15	10.37	25.73	1.244	1.399
333.15	11.02	26.02	1.296	1.451
343.15	11.53	33.04	1.322	1.685
353.15	11.92	33.33	1.399	1.840

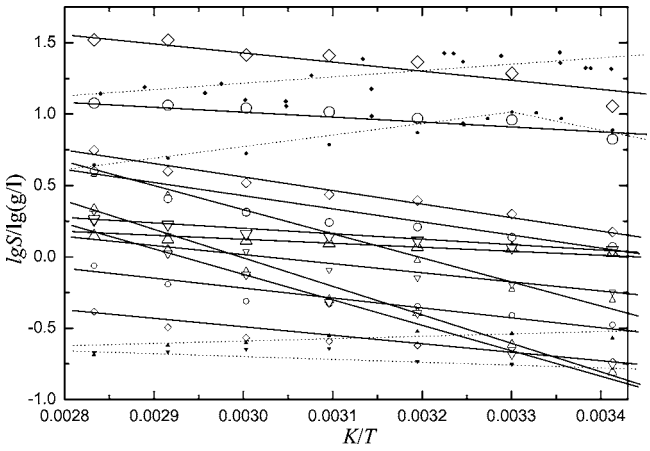

Figure 18. Comparative data on the solubility of C_{60} and $C_{60}Br_n$, n = 6, 8, and 24, in *o*-xylene, *o*-dichlorobenzene, *n*-decanol-1, and heptanoic acid in the temperature range (293 to 353) K. °, $C_{60}Br_{24}$ + *o*-xylene; ○, $C_{60}Br_8$ + *o*-xylene; ○, $C_{60}Br_6$ + *o*-xylene; ●, C_{60} + *o*-xylene; ◇, $C_{60}Br_{24}$ + *o*-dichlorobenzene; ◇, $C_{60}Br_8$ + *o*-dichlorobenzene; ◇, $C_{60}Br_6$ + *o*-dichlorobenzene; ♦, C_{60} + *o*-dichlorobenzene; △, $C_{60}Br_{24}$ + decan-1-ol; Δ, $C_{60}Br_8$ + decan-1-ol; ▲, $C_{60}Br_6$ + decan-1-ol; ▲, C_{60} + decan-1-ol; ▽, $C_{60}Br_{24}$ + heptanoic acid; ∇, $C_{60}Br_8$ + heptanoic acid; ∇, $C_{60}Br_6$ + heptanoic acid; ▼, C_{60} + heptanoic acid.

derivative) in various solvents are also presented. Moreover, in the context of this review, the authors have investigated the solubility of individual light fullerenes and industrial fullerene mixture in oleic acid, oleinic acid, and linolenoic acid as well as solubility of fullerenes in the ternary system C_{60} + C_{70} + 1,2-dichlorobenzene at 423 K.

Supporting Information Available:

Additional data for Tables 1, 2, 3, 6, and 7.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review March 29, 2009. Accepted September 15, 2009.

JE900296S