# Solubility of Bromoderivatives $C_{60}Br_n$ ($n = 6, 8, 24$) in 1-Chloronaphthalene and 1-Bromonaphthalene in the Temperature Range (10 to 60) °C

**Konstantin N. Semenov,*[†] Nikolai A. Charykov,[†,‡] and Boris M. Axel'rod[†]**

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

On the basis of the isothermal saturated method in ampules, the solubility of bromoderivatives $C_{60}Br_n$ ($n =$ 6, 8, 24) in 1-chloronaphthalene and 1-bromonaphthalene in the (10 to 60) °C temperature range was determined. The temperature dependencies of solubility and density are presented and characterized, and the compositions of equilibrium solid phases are determined.

## Introduction

Analysis of the literature data presents a great number of experimental data concerning solubility of the individual light fullerenes in the solvents of different physical nature (for example, the latest review presents more than 90 original references on solubility of fullerenes[1]). In spite of this fact, the data on solubility of fullerene derivatives are extremely limited. The data on isothermal and polythermal solubility of light fullerene derivatives in various solvents are few in number.

Tian et al. 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*-dichlorobenzene, 1,2,4-dichlorobenzene, bromobenzene, iodobenzene, and dichloromethane) at 20 °C.[2−4] Authors also described a 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. Authors of ref 5 have synthesized the bromine derivatives of $C_{60}$ ($C_{60}Br_n$, $n =$ 6, 8, 24) and studied their solubility in *o*-xylene, *o*-dichlorobenzene, 1-decanol, and heptanoic acid in the temperature range (20 to 80) °C. Finally, the solubility of the bromoderivatives of the $C_{60}$ fullerene ($C_{60}Br_n$, $n =$ 6, 8, 24) in the binary water + ethanol solvent mixtures in the whole concentration range at 25 °C was studied in our group.[6]

Investigation of solubility in $C_{60}Br_n$ ($n =$ 6, 8, 24) + 1-$C_{10}H_7Cl$ and $C_{60}Br_n$ + 1-$C_{10}H_7Br$ systems is actual due to the following reasons: for the addition of the experimental data on phase solid−liquid equilibrium in the systems including bromoderivatives of the light fullerenes, it is known that the individual light fullerenes have higher solubility in halogen naphthalenes (1-$C_{10}H_7Cl$ and 1-$C_{10}H_7Br$) than in other investigated solvents. For instance, the solubility of the $C_{60}$ fullerene in 1-$C_{10}H_7Cl$ at 25 °C is equal to (51 to 52) g,[1,7,8] and from general considerations we have proposed that the solubility of bromoderivatives in halogen naphthalenes would be high (from (1 to 10) g of fullerenes per liter of solvent). In addition, the solubility of $C_{60}Br_n$ in monohalogenonaphthalenes should increase with increasing temperature, and the latest fact was observed in ref 5. Another fullerene derivative (for example, the fullerols, $C_{60}(OH)_n$) can be obtained from the highly soluble bromoderivatives of the $C_{60}$ fullerene.[9,10] Finally, the soluble bromoderivatives $C_{60}Br_n$ ($n =$ 6, 8, 24) can be effectively used in carrying out the (inter)polymerization (≪stitching≫) of fullerenes based on the Fittig−Wurtz reaction. Using the bromoderivative solutions in halogen naphthalenes with mass concentration not less than units percents for such synthesis is very convenient.[11]

## Experimental Section

Fullerene $C_{60}$ had a mass fraction purity of 99.9 %, with the main detectable impurity $C_{70}$ ($\omega = 0.001$). The reagent was produced at ZAO "ILIP" (St. Petersburg). The other reagents used were reagent grade molecular $Br_2$, anhydrous $FeBr_3$, 1-bromonaphthalene, and 1-chloronaphthalene (purchased from Vecton Ltd., St.-Petersburg).

The $C_{60}Br_6$ fullerene bromoderivative was synthesized as recommended in refs 12 and 14. $C_{60}$ (400 mg) was dissolved in *o*-dichlorobenzene (15 mL) at room temperature. The solution was filtered through a paper filter to remove traces of undissolved fullerene, and a 1000-fold excess of molecular $Br_2$ (≈1.1 mL) was added to it. The solution was allowed to stand at room temperature for several days, filtered, and washed with hexane (2 mL) and dichloromethane (2 mL). Excess $Br_2$ and *o*-dichlorobenzene were then distilled off in a vacuum desiccator at room temperature and residual pressure of 1.3 Pa. The product was brown−black finely dispersed powder of the $C_{60}Br_6$ $0.5Br_2 \cdot 0.5C_6H_4(CH_3)_2$ mixed solvate, whose composition was substantiated gravimetrically (by calcining in a vacuum at ≈100 °C).

$C_{60}Br_8$ bromofullerene was synthesized following ref 12. $C_{60}$ (150 mg) was dissolved in liquid $Br_2$ (10 mL).The solution was left to stand at room temperature for (15 to 30) min and filtered through a paper filter, and excess $Br_2$ was distilled off in a vacuum desiccator. The yield was almost quantitative. The product was dark brown finely dispersed $C_{60}Br_8$ $2Br_2$ disolvate powder, whose composition was substantiated gravimetrically.

---

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

10.1021/je100224a

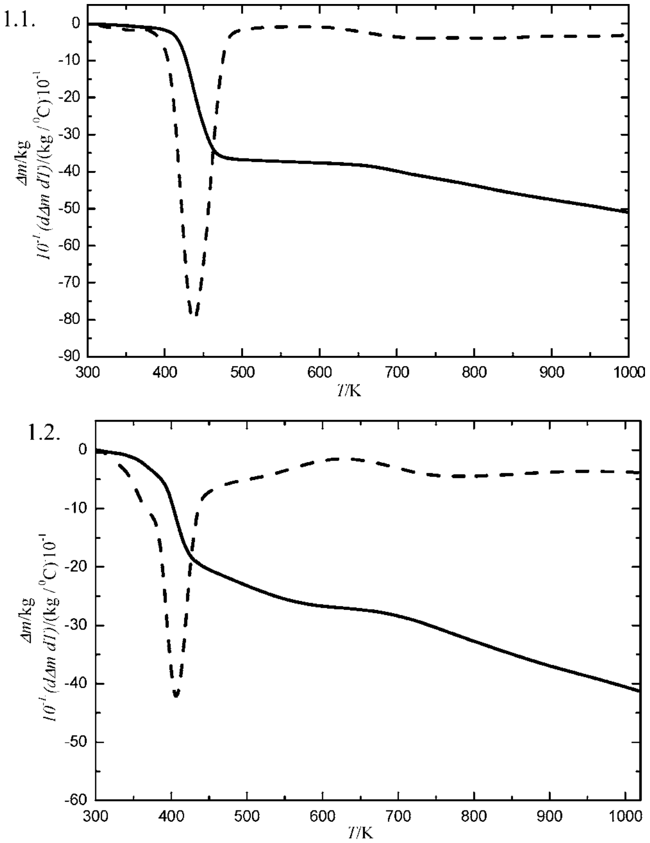

**Figure 1.** Derivatograms of $C_{60}Br_n$, $n = 24$ (1.1) and 8 (1.2), obtained in air at a 10 K·min$^{-1}$ heating rate: solid line, thermogravimetric curve; dashed line, differential thermogravimetric curve.

$C_{60}Br_{24}$ bromofullerene was synthesized as described in ref 13. $C_{60}$ (300 mg) was dissolved in a small excess of liquid $Br_2$ ($\approx$2 mL). $FeBr_3$ catalyst (50 mg) was added to the solution, and the solution was stirred for 40 min and filtered through a paper filter. Excess $Br_2$ was distilled off in a vacuum desiccator at room temperature, and the solid phase was washed with a volume fraction of 0.3 ethanol in water aqueous ethanol. The yield was almost quantitative. The product was orange finely dispersed $C_{60}Br_{24}$ $Br_2$ monosolvate powder. Its composition was substantiated gravimetrically.

Bromofullerene solvates $C_{60}Br_n$ $m$$Br_2$ ($n = 6, 8, 24$; $m = 0.5, 2, 1$) were identified by recording the IR spectra of solid products. The spectra were obtained on a SHIMADZU FTIR 8400S instrument. They were close to those reported in the literature. $C_{60}Br_n$ bromofullerene solvates were also indentified thermogravimetrically on a Q_-1500 derivatograph (Hungary). These measurements substantiated the preparation of individual substances. By way of example, the derivatograms of $C_{60}Br_{24}$ and $C_{60}Br_8$ obtained in open volume in air at a 10 K·min$^{-1}$ heating rate are shown in Figure 1. At (164 ± 3) °C and (135 ± 3) °C, $C_{60}Br_{24}$ and $C_{60}Br_8$ dissociate with almost complete vaporization of $Br_2$, and the remaining "decomposed $C_{60}$" experiences oxidation and vaporizes, also almost completely, at temperatures up to 1000 °C. Similar results were obtained for $C_{60}Br_6$.

***Method of Investigation of Solubility.*** Experimental studies of the temperature dependence of the solubility of brominated fullerenes $C_{60}Br_n$ ($n = 6, 8, 24$) were performed by the isothermal saturation method in ampules. Solutions of $C_{60}Br_n$ ($n = 6, 8, 24$) in the solvents specified above (in all experiments, fullerenes were taken in substantial excess, 1000 mg per 10 mL of the solvent) were saturated at (10 to 60) °C in a temperature-controlled shaker (temperature was maintained with an accuracy of ± 0.05 K) for 10 h at each temperature. The long duration of the experiment is connected with the long duration of the equilibrium state in the concerned systems ($C_{60}$, $C_{70}$, fullerene mixture−solvent). In all cases, the dissolution kinetics of the bromoderivatives in 1-chloro(bromo)naphthalenes was investigated for determination of the average time necessary for saturation of the solutions. The experimental method for determination of the solvent content in solid crystal solutes was as follows. The solid phase, deposited from 1-chloro(bromo)naphthalene solution, was filtered through a Schott filter (porosity factor of 10), rinsed fast by ethanol, and then dried for 10 to 15 min at 20 °C. Then the solid phase was subsequently weighed, repeatedly washed with methanol in a Soxhlete apparatus at 78 °C, 1 atm, dried for 1 h in vacuum (0.1 Torr) at 200 °C, and weighed again. The weight change corresponded to the solvent content in the initial crystal solutes. $C_{60}Br_n \cdot n_1 1\text{-}C_{10}H_7Cl$ and $C_{60}Br_n \cdot n_2 1\text{-}C_{10}H_7Br$ bromofullerene solvates were also indentified thermogravimetrically on a Q-1500 derivatograph (Hungary) in open volume with a 10 °C per minute heating rate. The results of both methods agreed well. As a result, we obtained the following figures, concerning the content of solvent molecules ($1\text{-}C_{10}H_7Cl$ and $1\text{-}C_{10}H_7Br$) in solid crystal−solvates ($C_{60}Br_n \cdot n_1 1\text{-}C_{10}H_7Cl$ and $C_{60}Br_n \cdot n_2 1\text{-}C_{10}H_7Br$): in all cases (if $n = 6, 8, 24$) $n_1 \approx n_2 \approx 1.0 \pm 0.2$ (figures are in conditional molecular units).

***Spectrophotometric Method of Determination of Bromoderivative Concentrations in 1-Chloronaphthalene and 1-Bromonaphthalene.*** Concentrations after each stage of saturation with $C_{60}Br_n$ ($n = 6, 8, 24$) were determined spectrophotometrically on a Specord-32 spectrophotometer at $\lambda = (335 \text{ to } 340)$ nm. The accuracy of wavelength maintenance was ± 0.5 nm; photometric accuracy ($\Delta D$) was equal to ± 0.005 (a.u.); and the absorption layer was 1 cm thick. The extinction coefficients of $C_{60}Br_n$ ($n = 6, 8, 24$) at this wavelength were determined preliminarily. $C_{60}Br_n$ ($n = 6, 8, 24$) samples were dissolved in excess amounts of 1-chloronaphthalene and 1-bromonaphthalene, and the electronic absorption spectra of the solutions were recorded and studied. The absorption spectra of $C_{60}Br_n$ ($n = 6, 8, 24$) in 1-chloronaphthalene and 1-bromonaphthalene are presented in Figures 2.1 and 2.2. Figure 2 reveals that solutions of $C_{60}Br_n$ in all solvents exhibit well-defined absorption bands at $\lambda = (335 \text{ to } 340)$ nm in the visible and near UV range. The latest fact is agreed well with the previous study on investigation of solubility and electronic spectra of bromofullerenes in *o*-xylene, *o*-dichlorobenzene, enanthic acid, and *n*-decanol-1. The authors of ref 5 determined the presence of an absorption band at $\lambda \approx 330$ nm in all investigated systems of $C_{60}Br_n$ ($n = 6, 8, 24$), *o*-xylene, *o*-dichlorobenzene, enanthic acid, and *n*-decanol-1.

Irrespective of the solvent ($1\text{-}C_{10}H_7Cl$ and $1\text{-}C_{10}H_7Br$), the concentrations of $C_{60}Br_n$ can be calculated as

$$C(C_{60}Br_6)/[\text{mg}\cdot\text{L}^{-1}] = 12.1D_{340}[1\text{ cm}] \qquad (1)$$

$$C(C_{60}Br_8)/[\text{mg/L}^{-1}] = 16.2D_{340}[1\text{ cm}] \qquad (2)$$

$$C(C_{60}Br_{24})/[\text{mg/L}^{-1}] = 55.9D_{340}[1\text{ cm}] \qquad (3)$$

where C($C_{60}Br_n$) is the concentration of $C_{60}Br_n$ in mg·L$^{-1}$, and $D_{340}$ is the optical density of the $C_{60}Br_n$ solution at a spectrophotometric cell thickness of 1 cm and wavelength $\lambda = (335$ to

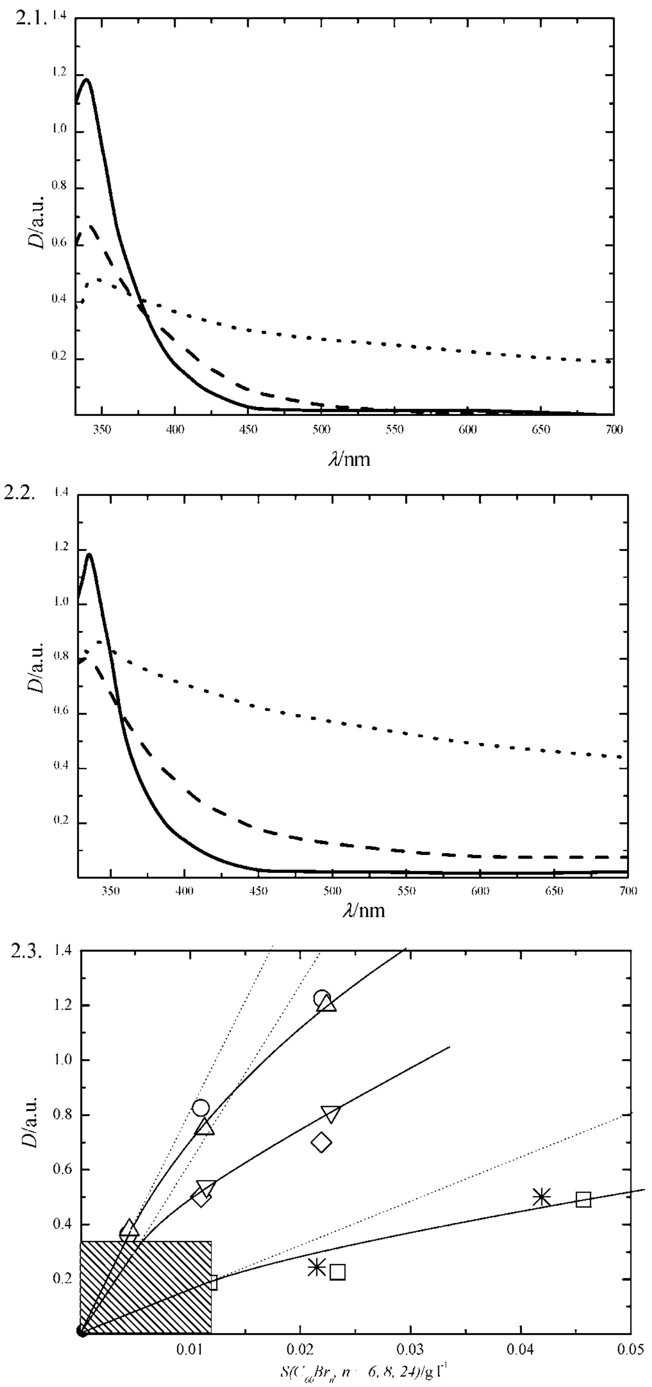

**Figure 2.** Optical spectra of the $C_{60}Br_6$ (solid line), $C_{60}Br_8$ (dashed line), and $C_{60}Br_{24}$ (dotted line) solutions in 1-$C_{10}H_7Cl$ (2.1) and 1-$C_{10}H_7Br$ (2.2). $D$ is optical density; $\lambda$ is wavelength. Dependencies of the optical densities of solutions of $C_{60}Br_n$ ($n$ = 6, 8, 24) in 1-chloronaphthalene and 1-bromonaphthalene on solution concentrations at $\lambda$ = 340 nm (thickness of absorption layer is equal to 1 cm). ○, $C_{60}Br_6$ + 1-chloronaphthalene; ◊, $C_{60}Br_8$ + 1-chloronaphthalene; □, $C_{60}Br_{24}$ + 1-chloronaphthalene; Δ, $C_{60}Br_6$ + 1-bromonaphthalene; ▽, $C_{60}Br_8$ + 1-bromonaphthalene; ∗, $C_{60}Br_{24}$ + 1-bromonaphthalene. Shadowed area corresponds to the validity of the Bouger−Beer−Lambert law (2.3).

340). Figure 2.3 shows how the Bouger−Beer−Lambert law holds for solutions of $C_{60}Br_n$ ($n$ = 6, 8, 24) in 1-chloronaphthalene and 1-bromonaphthalene. We see that the law is valid over the range of solution optical densities $D \leq 0.2$ to 0.4, which allows eqs 1 to 3 to be used for calculations only in this diapason. The overall accuracy of determining concentrations of light fullerenes ($C_{60}$ and $C_{70}$) in a saturated solution is no more than 5 %.

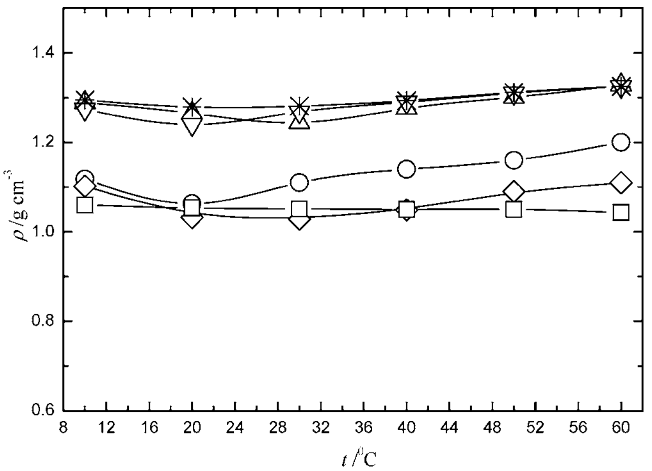

**Figure 3.** Temperature dependencies of density of $C_{60}Br_n$ ($n$ = 6, 8, 24) in 1-chloronaphthalene and 1-bromonaphthalene in the temperature range from (10 to 60) °C. ○, $C_{60}Br_6$ + 1-chloronaphthalene; ◊, $C_{60}Br_8$ + 1-chloronaphthalene; □, $C_{60}Br_{24}$ + 1-chloronaphthalene; Δ, $C_{60}Br_6$ + 1-bromonaphthalene; ▽, $C_{60}Br_8$ + 1-bromonaphthalene; ∗, $C_{60}Br_{24}$ + 1-bromonaphthalene.

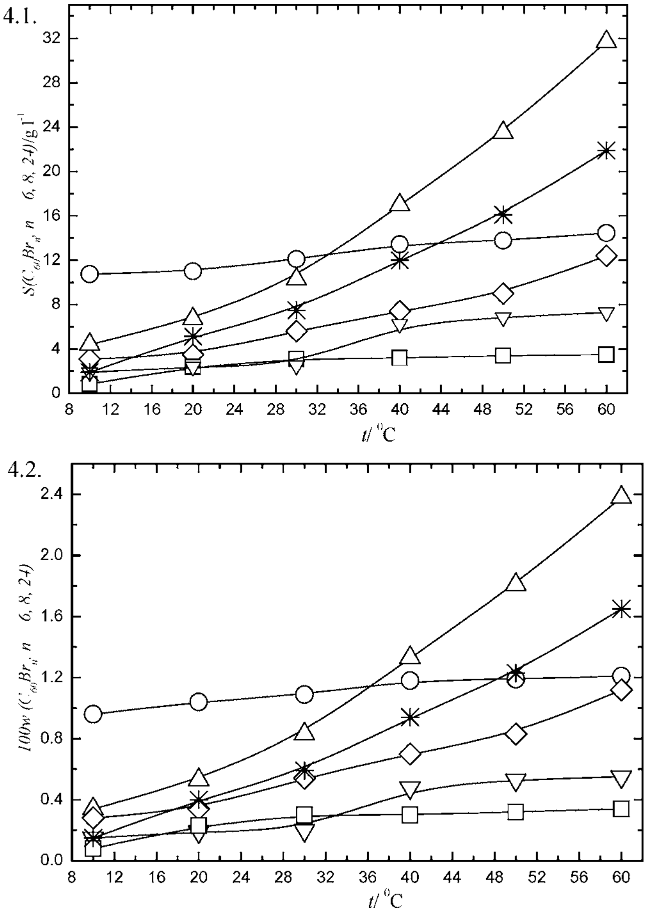

**Figure 4.** Solubility of $C_{60}Br_n$ ($n$ = 6, 8, 24) in 1-chloronaphthalene and 1-bromonaphthalene in two concentration scales: volume concentrations (4.1) and bulk mass concentrations (4.2) (temperature range from (10 to 60) °C). ○, $C_{60}Br_6$ + 1-chloronaphthalene; ◊, $C_{60}Br_8$ + 1-chloronaphthalene; □, $C_{60}Br_{24}$ + 1-chloronaphthalene; Δ, $C_{60}Br_6$ + 1-bromonaphthalene; ▽, $C_{60}Br_8$ + 1-bromonaphthalene; ∗, $C_{60}Br_{24}$ + 1-bromonaphthalene.

***Method of Determination of Densities of the $C_{60}Br_n$ Solutions in Monohalogenonaphthalenes.*** The bottle method was used for the determination of densities of the saturated $C_{60}Br_n$ ($n$ = 6, 8, 24), monohalogenonaphthalene (1-$C_{10}H_7Cl$ and 1-$C_{10}H_7Br$) solutions.[15] The data were obtained by weight-

**Table 1. Solubility of Bromoderivatives $C_{60}Br_n$ ($n = 6, 8, 24$) in 1-$C_{10}H_7Cl$ and 1-$C_{10}H_7Br$ in the Temperature Range (10 to 60) °C**[a]

| | | | *t*/°C | | | | | |
|---|---|---|---|---|---|---|---|---|
| compd | solvent | parameters | 10 | 20 | 30 | 40 | 50 | 60 |
| $C_{60}Br_6$ | 1-chloronaphthalene | $\rho/g\cdot cm^{-3}$ | 1.12 | 1.06 | 1.11 | 1.14 | 1.16 | 1.20 |
| | | $S_{C_{60}Br_n}/g\cdot L^{-1}$ | 10.8 | 11.0 | 12.1 | 13.4 | 13.8 | 14.5 |
| | | $100\ w$ | 0.96 | 1.04 | 1.09 | 1.18 | 1.19 | 1.21 |
| | 1-bromonaphthalene | $\rho/g\cdot cm^{-3}$ | 1.29 | 1.27 | 1.24 | 1.28 | 1.30 | 1.33 |
| | | $S_{C_{60}Br_n}/g\cdot L^{-1}$ | 4.4 | 6.7 | 10.3 | 17.0 | 23.5 | 31.7 |
| | | $100\ w$ | 0.34 | 0.53 | 0.83 | 1.33 | 1.81 | 2.38 |
| $C_{60}Br_8$ | 1-chloronaphthalene | $\rho/g\cdot cm^{-3}$ | 1.10 | 1.03 | 1.03 | 1.05 | 1.09 | 1.11 |
| | | $S_{C_{60}Br_n}/g\cdot L^{-1}$ | 3.1 | 3.5 | 5.6 | 7.4 | 9.0 | 12.4 |
| | | $100\ w$ | 0.28 | 0.34 | 0.54 | 0.70 | 0.83 | 1.12 |
| | 1-bromonaphthalene | $\rho/g\cdot cm^{-3}$ | 1.27 | 1.24 | 1.27 | 1.29 | 1.31 | 1.33 |
| | | $S_{C_{60}Br_n}/g\cdot L^{-1}$ | 1.9 | 2.4 | 2.5 | 6.2 | 6.9 | 7.3 |
| | | $100\ w$ | 0.15 | 0.19 | 0.20 | 0.48 | 0.53 | 0.55 |
| $C_{60}Br_{24}$ | 1-chloronaphthalene | $\rho/g\cdot cm^{-3}$ | 1.06 | 1.05 | 1.05 | 1.05 | 1.05 | 1.04 |
| | | $S_{C_{60}Br_n}/g\cdot L^{-1}$ | 0.85 | 2.4 | 3.1 | 3.2 | 3.4 | 3.5 |
| | | $100\ w$ | 0.080 | 0.23 | 0.30 | 0.30 | 0.32 | 0.34 |
| | 1-bromonaphthalene | $\rho/g\cdot cm^{-3}$ | 1.30 | 1.28 | 1.28 | 1.29 | 1.31 | 1.33 |
| | | $S_{C_{60}Br_n}/g\cdot L^{-1}$ | 1.9 | 5.1 | 7.6 | 12.1 | 16.1 | 21.9 |
| | | $100\ w$ | 0.15 | 0.40 | 0.59 | 0.94 | 1.23 | 1.65 |

[a] $\rho$, density of the $C_{60}Br_n$ saturated solution; $S_{C_{60}Br_n}$, volume concentration of the $C_{60}Br_n$ bromoderivative; $C_{C_{60}Br_n}$, mass fraction of the $C_{60}Br_n$ bromoderivative.

ing of a quartz volumetric flask invaded by a saturated solution of $C_{60}Br_n$ at controlled temperature (Table 1). The volume of the volumetric flask was determined in terms of the data on mass of water and density of water at fixed temperature. The data on the temperature dependence of density of water at 1 atm were taken from ref 16. The accuracy of the density determination is no more than 2 % or about 0.025 $g\cdot L^{-1}$. Apart from everything else, the uncertainty is connected with the thermostat control accuracy especially at temperatures higher than 20 °C.

## Results and Discussion

The temperature dependencies of density of saturated solutions of $C_{60}Br_n$ ($n = 6, 8, 24$) in monohalogenonaphthalenes (1-$C_{10}H_7Cl$ and 1-$C_{10}H_7Br$) in the temperature range (10 to 60) °C are presented in Figure 3 and Table 1. Figure 3 reveals the complex and extreme temperature dependencies of density of the saturated solutions; moreover, the densities of the $C_{60}Br_n$ ($n = 6, 8, 24$) solutions in 1-$C_{10}H_7Cl$ and 1-$C_{10}H_7Br$ converge to densities of the corresponding pure halogenonaphthalene.

The comparatively complex shape of the temperature dependencies of density curves can be explained in terms of the following factors:

- With an increase of temperature, the densities of solute bromo derivatives $C_{60}Br_n$ ($n = 6, 8, 24$) strongly decrease. These data are also absent in the literature.
- Finally, with an increase of temperature, the solubility values of bromofullerenes $C_{60}Br_n$ in bromonaphthalenes vary in both concentration scales (volume and weight). The temperature dependencies of $C_{60}Br_n$ solubility in monohalogenonaphthalenes in volume and weight concentration scales are presented in Figures 4.1 and 4.2 correspondingly. Figure 4 reveals the following regularities:
- The $C_{60}Br_n$ solubility in monohalogenonaphthalenes varies from 1 $g\cdot L^{-1}$ to 10 $g\cdot L^{-1}$ and from 0.001 to 0.01 in mass fraction scale. Furthermore, the $C_{60}Br_n$ solubility in monohalogenonaphthalenes considerably and monotonously increases with increasing temperature.

The following order of the temperature dependencies of solubility takes place in both concentration scales (volume and mass):

(a) for the 1-$C_{10}H_7Cl$ solutions: $S(C)$ ($n = 6$) > $S(C)$ ($n = 8$) > $S(C)$ ($n = 24$)

(b) for the 1-$C_{10}H_7Br$ solutions: $S(C)$ ($n = 6$) > $S(C)$ ($n = 24$) > $S(C)$ ($n = 8$).

At comparatively high temperatures, the $C_{60}Br_n$ solubility in 1-$C_{10}H_7Cl$ is higher (by several times) than solubility values in 1-$C_{10}H_7Cl$. On the contrary, at comparatively low temperatures, the $C_{60}Br_n$ solubility values in 1-$C_{10}H_7Cl$ are higher than solubility in 1-$C_{10}H_7Br$.

## Conclusions

The authors have investigated the solubility in binary systems of bromoderivatives $C_{60}Br_n$ ($n = 6, 8, 24$), 1-chloronaphthalene and 1-bromonaphthalene. Temperature dependencies of solubility and density are presented and characterized, and the relevance of this kind of research is discussed. We have established that light fullerenes and solid solutions based on them form the solid crystal solvates which contain molecules of the corresponding solvent.

### Supporting Information Available:

IR spectra of $C_{60}Br_n$ ($n = 6, 8, 24$). This material is available free of charge via the Internet at http://pubs.acs.org.

## Literature Cited

(1) Semenov, K. N.; Charykov, N. A.; Keskinov, V. A.; Blokhin, A. A.; Kopyrin, A. A. Solubility of Light Fullerenes in Organic Solvents. *J. Chem. Eng. Data* **2009**, *55*, 13–36.

(2) Tian, J. Comparative solubility study of $C_{60}$ and $C_{60}$-piperazine and applications on quartz crystal microbalance/heat conduction calorimeter. A Thesis Submitted to the Faculty of Drexel University by Jun Tian in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 2002.

(3) Tian, J.; Li, D.; Smith, A. L.; Korobov, M. V.; Stukalin, E. B.; Avramenko, N. V. Solubility and Solvate Formation For a Fullerene Derivative: the $C_{60}$-Piperazine Monoadduct. *Proc. Electrochem. Soc.* **2000**, *12*, 121–128.

(4) Tian, J.; Li, D.; Smith, A. L.; Korobov, M. V.; Stukalin, E. B.; Avramenko, N. V. Solubility and Solvate Formation For a Fullerene Derivative: the $C_{60}$-Piperazine Monoadduct. *Proc. Electrochem. Soc.* **2000**, *12*, 121–128.

(5) Semenov, K. N.; Charykov, N. A.; Keskinov, V. A.; Pjartman, A. K.; Jakovlev, V. V.; Arapov, O. V. Solubility of $C_{60}Br_n$ (n = 6, 8, 24) in various solvents. *Russ. J. Phys. Chem.* **2009**, *11*, 1935–1939.

(6) Semenov, K. N.; Charykov, N. A.; Keskinov, V. A.; Pjartman, A. K.; Arapov, O. V. Solubility of $C_{60}Br_n$ (n = 6, 8, 24) in water - ethanol mixtures at 25°C. *Russ. J. Appl. Chem.*, in print.

(7) Ruoff, R. S.; Tse, D.; Malhorta, R.; Lorents, D. C. Solubility of fullerene $C_{60}$ in a variety of solvents. *J. Phys. Chem.* **1993**, *97*, 3379–3383.

(8) Avramenko, N. V.; Stukalin, E. B.; Korobov, M. V. Thermodynamic properties of the molecular complexes of $C_{60}$ with monosubstituted naphthalenes. *J. Therm. Anal. Calorim.* **2005**, *82*, 125–127.

(9) Pinteala, M.; Dascalu, A.; Ungurenasu, C. Binding fullerenol $C_{60}(OH)_{24}$ to dsDNA. *Int. J. Nanomed.* **2009**, *4*, 193–199.

(10) Li, J.; Takeuci, A.; Ozawa, M.; Li, X.; Saigo, K.; Kitazawa, K. $C_{60}$ Fullerol formation catalyst by quaternary ammonium hydroxides. *J. Chem. Soc., Chem. Commun.* **1993**, *23*, 1784–1786.

(11) Ter-Gabrieljam, E. G. *Reactions of the metalloorganic compounds as a reduction-oxidation processes*; Khimija: Moscow, 1981.

(12) Troshin, P. A.; Kolesnikov, D.; Burtsev, A. V.; Lubovskaya, R. N.; Denisenko, N. I.; Popov, A. A.; Troyanov, S. I.; Boltalina, O. V. Bromination of [60] Fullerene. I. High-Yield Synthesis of $C_{60}Br_x$ ($x = 6, 8, 24$). *Fullerenes, Nanotubes, Carbon Nanostruct.* **2003**, *11*, 47–60.

(13) Djordjevie, A.; Vojinovic-Miloradov, M.; Petranovic, N.; Devecerski, A.; Lazar, D.; Ribar, B. Catalytic Preparation and Characterization of $C_{60}Br_{24}$. *Fullerenes, Nanotubes, Carbon Nanostruct.* **1998**, *6*, 689–694.

(14) Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. Preparation and characterization of $C_{60}Br_6$ and $C_{60}Br_8$. *Nature.* **1992**, *357*, 479–481.

(15) Stromberg, A. G. *Physical Chemistry*; Visshaja Shkola: Moscow, 1973.

(16) Mischenko, K. P.; Ravdel', A. A. *Abstract of physical-chemical properties*; Khimija: Leningrad, 1974.

Received for review March 10, 2010. Accepted July 25, 2010. The work was supported by the Government of Saint-Petersburg (grant N 2.5/04 − 05/177).

JE100224A