Density, specific heat capacity and viscosity of fullerene C$_{60}$ solutions in tetralin

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Abstract. By combination of thermophysical and optical properties the solutions of tetralin with nanoparticles such as fullerene C$_{60}$ can be considered as promising heat transfer agents for solar energy. The paper presents the results of experimental investigation for the density, viscosity and specific heat capacity of tetralin / fullerene C$_{60}$ solutions. The study was performed in the temperature range 237...434 (K) and concentrations of fullerene C$_{60}$ up to 1.043 (wt.%). The obtained results have shown an increase in the density and viscosity, as well as a decrease in the specific heat capacity of tetralin after adding C$_{60}$. The obtained temperature dependences for the thermophysical properties of tetralin / C$_{60}$ solutions are equidistant to theirs for tetralin. Obtained data on the density and viscosity were accurately fitted by a few-constant correlations for non-associated substances. The experimental data on the specific heat capacity of both tetralin and tetralin / C$_{60}$ solutions indicate to significant effect of supramolecular structures in a liquid phase of aromatic hydrocarbons on this property. This effect is most significant in the temperature region close to the triple point. A new correlation for predicting the specific heat capacity of aromatic hydrocarbons containing fullerene C$_{60}$ on the boiling line using a limited initial empirical data is proposed.

1. Introduction
One of the promising directions for increasing the efficiency of solar power systems is using of nanofluids instead of traditionally applied heat transfer agents. To achieve the maximum efficiency of direct absorption solar power systems, the researchers pay considerable attention both to studying thermophysical and optical properties of the heat transfer agents and the heat transfer during a forced convection in heat exchangers. The use of a nanotechnology allows purposefully changing the thermophysical properties of the high-temperature heat transfer agents and regulating the efficiency of a sunlight absorption by the use of the hybrid nanofluids [1]. In addition, the presence of nanoparticles in the heat transfer agent can contribute to increasing the intensity of heat transfer in the solar power systems heat transfer equipment, reducing the mass-size characteristics of it and reducing power costs of heat transfer agent pumping. Therefore, the aim of present study is examination of influence of the additives of nanoparticles fullerene C$_{60}$ on the thermophysical and optical properties of the prospect heat transfer agent for solar power systems. Tetralin due to the combination of its thermophysical properties and high ability to dissolve fullerene can be considered as a promising high-temperature heat transfer agent for direct absorption solar energy systems. However, the optical and thermophysical properties of tetralin / fullerene C$_{60}$ solutions remain poorly investigated. The paper presents the results of the experimental study of the density, viscosity and heat capacity of
tetralin / fullerene C₆₀ solutions in the temperature range from 237 to 434 (K) and the concentration range of C₆₀ up to 1.015 (wt.%).

2. Experiment

2.1. Materials, samples preparation and stability investigation

The samples of tetralin / fullerene C₆₀ solutions were prepared from following components: tetralin (1,2,3,4-tetrahydronaphthalene, manufacturer Sigma Aldrich, CAS # 119-64-2, purity 99 (wt.%)); fullerene C₆₀ (manufacturer Suzhou Dade Carbon Nanotechnology Co., CAS # 99685-96-8, purity 99.5 (wt.%)).

The solubility of fullerene C₆₀ in tetralin is well studied and ranges from 0.017 to 0.022 (mol dm⁻³) (0.0126 to 0.0163 (kg kg⁻¹)) at 298 (K) according to authors [2, 3]. All examined samples had a concentration of C₆₀ in tetralin lower than a saturation concentration. It was shown in [4] that at these concentrations only molecular solutions are formed.

The samples of tetralin / C₆₀ solutions were prepared using a two-stage method for preparing the nanofluids. The solutions were sonicated for three hours using a submersible ultrasonic generator UZG 13-0.1/22 (frequency 22 (kHz), power 0.1 (kW)). The mass concentration of the components in solutions determined by a weighing method using an electronic analytical scales AND GR-300 (accuracy 0.5 (mg)).

In order to analyze the effect of C₆₀ concentration on the light absorption capacity of tetralin / C₆₀ solutions, the study of a spectral absorbance was performed. The spectral dependence of the absorbance was determined using a Shimadzu UV-1700 scanning spectrophotometer in a quartz plane-parallel cell with an optical path length of 10 (mm) at the temperature of 290 (K).

Figure 1 shows that tetralin / C₆₀ solutions with the relative low C₆₀ concentrations have a good light absorption capacity at wavelengths up to 700 nm. Therefore, tetralin / C₆₀ solutions can be considered as the base fluids for preparation of the hybrid heat transfer agents for direct absorption solar energy [1]. Repeated measurements of the absorbance (every 3-7 days for 6 months) at a wavelength of 630 (nm) confirmed the excellent stability of the solutions of fullerene C₆₀ in tetralin at all investigated concentrations (value of the absorbance did not change in time).

![Figure 1. Spectral dependence of the light absorbance of fullerene C₆₀ in tetralin solutions at the different mass concentrations of C₆₀.](image)

2.2. Measurement technique

The density of tetralin / C₆₀ solutions was measured using a variable volume pycnometer method. The range of the measured volumes of the pycnometer covers the values from 2.4 to 2.8 (cm³). For a calibration of the pycnometer was used distilled, deaerated water, that density data are given in [5].

The obtained values of the pycnometer volume depended from the liquid level height were fitted by a linear dependence.
\[ V'(\Delta h) = a \cdot \Delta h - b, \]  

where \( V'(\Delta h) \) is the volume of the liquid in the pycnometer, (cm\(^3\)); \( \Delta h \) is the height of the liquid column in the pycnometer, mm; \( a = 0.00300821 \) and \( b = 2.373699007 \) are the fitting coefficients.

The pycnometer with nanofluid sample was placed in the liquid thermostat equipped with an automatic temperature control system. The temperature fluctuations did not exceed 0.02 (K). The temperature was measured by a platinum resistance thermometer. The density measurements were performed at the following concentrations of fullerene \( C_{60} \) in tetralin: 0.1997, 0.4922 and 0.7017 (wt.\%) in the temperature range 280-360 (K).

The kinematic viscosity of tetralin / \( C_{60} \) solutions was determined by a Ubbelode viscometer. The viscosity was measured for the following mass concentrations of \( C_{60} \) in solutions: 0.2505, 0.4922 and 0.7017 (wt.\%) in the temperature range 300-440 (K).

Since density and viscosity measurements were performed in a wide temperature range, measurement sells thermal deformation was taken into account at determining the viscometer constant and the pycnometer volume.

The investigation of two-phase specific isochoric heat capacity of tetralin/\( C_{60} \) solutions was performed by a continuous heating method in an adiabatic calorimeter. A detailed description of the experimental setup is given in [6]. The experiment included the specific heat capacity \( c_p \) measurements for pure tetralin and tetralin / \( C_{60} \) solutions with the following mass concentrations of \( C_{60} \): 0.501 and 1.043 (wt.\%) in the temperature range 237-330 (K). The adiabatic calorimeter was used in a monotonous heating mode, when all parameters were recorded every 6 seconds at the rate of temperature increase in the calorimeter from 0.0025 to 0.0030 (K·s\(^{-1}\)). The power supplied to the calorimeter remained below 0.5 (W). During the experiment, a zero temperature difference between a container with the test sample of tetralin / \( C_{60} \) solution and an adiabatic shell was maintained. The specific heat capacity was calculated by the formula

\[ c_V^{(2)} = c_p = \frac{P_{th} - P_{th}(T)}{m \cdot \Delta T / \Delta \tau} \cdot \frac{A(T)}{m}, \]  

where \( c_V^{(2)} \) is the specific isochoric heat capacity of a two-phase sample (at parameters significantly lower than tetralin normal boiling temperature it is equal to specific isobaric heat capacity at boiling line \( c_p \)), (J·kg\(^{-1}\)·K\(^{-1}\)); \( P_{th} \) is the average thermal power supplied to the calorimeter, (W); \( P_{th}(T) \) is the heat loss at the average temperature of the experiment, (W); \( \Delta T \) is the temperature change in the calorimeter, (K) during the time interval \( \Delta \tau \) (s); \( m \) is the mass of the test sample, kg; \( A(T) \) is the thermal value of the calorimeter at the average temperature of the experiment, (J·K\(^{-1}\)).

The thermal value of the calorimeter and heat loss at various temperatures were determined by the results of special calibration experiments [6].

### 3. Results

Performed analysis was shown that the presence of fullerene \( C_{60} \) do not significantly contribute to the tetralin thermophysical properties. Therefore, it is necessary to reduce the influence of the experimental data fitting error on the obtained effects of fullerene \( C_{60} \) on the tetralin density and viscosity. Proposed correlation for the density [7, 8] and Walter’s correlation for viscosity [9] correspond to this requirement. Unfortunately, few-constant correlations (that require a small amount of empirical data) for temperature dependence of the isobaric specific heat capacity on the boiling line are absent [10]. Therefore, a new correlation for description the experimental data on the isobaric heat capacity of tetralin/\( C_{60} \) solutions was proposed.

#### 3.1. Results of measurement

The experimentally obtained density data for tetralin / \( C_{60} \) solutions were fitted by few-constant correlations proposed in [7, 8]:
where $\Delta \rho$ is the difference between the densities of the test sample on the boiling and condensation lines, \((g\cdot m^{-3})\); $\rho_0$ and $B$ are the critical amplitude characterizing the individual properties of the substances, \((g\cdot m^{-3})\) and \((-\)) correspondently; $t = 1 - T/T_c$ is the reduced temperature, \((-\)) ; $T_c$ is the pseudocritical temperature, \((K)\); $T$ is the absolute temperature, \((K)\); $\omega' = \rho/\rho_0$ is the reduced density, \((-\)) ; $\Theta = \ln(T/T_c)$ is logarithm of the reduced temperature, \((-\)) ; $\beta$ is the critical index, $\beta = 0.325$; $F(t)$, $F_1(\Theta)$ is the crossover functions universal for non-associated substances, which values can be calculated using equations given in [7, 8].

The concentration dependences of the obtained coefficients $\rho_0$, $\tilde{\rho}_0$ and $T_c$ of equations (3) - (6) were fitted by relations listed in table 1. The performed analysis show that the value of $B$ was practically constant with variation of $C_{60}$ concentration ($B = 1.5312$).

The experimental data on the kinematic viscosity of tetralin / $C_{60}$ solutions were fitted by Walter equation

$$\ln[\ln(\nu - A(w_{C_{60}}))] = B(w_{C_{60}}) - C(w_{C_{60}}) \cdot \ln(T), \ (mm^2\cdot s^{-1}).$$

The obtained experimental data on the specific heat capacity of tetralin / $C_{60}$ solutions in the liquid phase were fitted by equation

$$c_p = A(w_{C_{60}}) + B(w_{C_{60}}) \cdot T^3, \ (J\cdot kg^{-1}\cdot K^{-1}).$$

The concentration dependences of the obtained coefficients of equations (3) - (6), (7) and (8) were fitted by relations listed in table 1.

Table 1. The values of the coefficients of the fitting equations (3) - (6), (7) and (8)

| Coefficients of the equations (3) - (6) | $T_c(w_{C_{60}}) = a + b \cdot \exp(-w_{C_{60}})$ | $\rho_0(w_{C_{60}}) = a + b \cdot w_{C_{60}}$ | $\tilde{\rho}_0(w_{C_{60}}) = a + b \cdot w_{C_{60}}$ |
|-----------------|-----------------|-----------------|-----------------|
| $a$             | 654.95          | 1.2352          | 0.34823         |
| $b$             | 4.0515          | 0.00735         | 0.02070         |

| Coefficients of the equation (7) | $A(w_{C_{60}}) = a + b \cdot (w_{C_{60}})^{0.5}$ | $B(w_{C_{60}}) = a + b \cdot (w_{C_{60}})^{0.5}$ | $C(w_{C_{60}}) = a + b \cdot (w_{C_{60}})^{0.5}$ |
|----------------|-----------------|-----------------|-----------------|
| $a$             | 0.797           | 9.327           | 3.906           |
| $b$             | 0.0382          | -0.613          | -0.247          |

| Coefficients of the equation (8) | $A(w_{C_{60}}) = a + b \cdot w_{C_{60}}$ | $B(w_{C_{60}}) = a + b \cdot w_{C_{60}}$ |
|----------------|-----------------|-----------------|
| $a$             | 1284.5          | 1.30 $10^{5}$   |
| $b$             | -47.02          | 1.05 $10^{6}$   |

where $a$ and $b$ are fitting coefficients; $w_{C_{60}}$ is the fullerene $C_{60}$ concentration, \((wt.\%)\).

3.2. Uncertainty analysis

The uncertainty analysis of determining the density, viscosity, and specific heat capacity of tetralin / $C_{60}$ solutions was performed in accordance with the recommendations presented in [11]. Both components of the uncertainty, type A “random” and type B “systematic”, were taken into account.
The calculations show that the uncertainty in determining the mass concentration of fullerenes in solutions did not exceed 0.8 (wt.%).

The expanded uncertainty of the temperature measurement at density and viscosity investigations did not exceed 0.05 (K).

The mass of the samples of tetralin / C₆₀ solutions and the empty pycnometer was determined on a GR-300 analytical balance, the uncertainty of the mass measurement did not exceed 0.0004 (g). The liquid level height of the samples filled into the pycnometer was measured by a KM-8 cathetometer with an uncertainty of 0.015 (mm). The expanded uncertainty of determining the pycnometer volume taking into account the error of the calibration fluid did not exceed 0.00051 (cm³). The analysis of the obtained experimental data shows that the expanded uncertainty in determining the density of the studied solutions did not exceed 0.00038 (g·cm⁻³).

The uncertainty of measuring the time of fluid flow in the viscometer did not exceed 0.1 (s).

According to the calculations, the expanded uncertainty in determining the viscosity did not exceed 0.00505 (mm²·s⁻¹).

The expanded standard uncertainty of determining the volume of the calorimeter cell at a given temperature (taking into account the thermal expansion of the cell) did not exceed 0.014 (cm³) (0.02%). The uncertainty of measuring the mass of the samples did not exceed on the average 10⁻⁶ (kg). The resistance thermometer installed inside the container was calibrated using a PTS −10 platinum resistance thermometer (R₀ ≈ 10 Ohm). The analysis shows that the expanded uncertainty of measuring the absolute temperature with a resistance thermometer did not exceed 0.02 (K). Giving some factors into account, in particular the temperature gradient in the sample, the expanded uncertainty of the absolute temperature measurements of the container with the sample did not exceed 0.03 (K). The total standard errors of determining the heat input did not exceed 2.5·10⁻⁵ (J) and the temperature difference 0.0045 (K). In this case, the expanded uncertainty of the specific heat capacity in the temperature range 237-330 (K) does not exceed 9.5 (J·kg⁻¹·K⁻¹) or 0.59 %.

4. Discussion

Figures 2-4 show the concentration dependences for the difference between the density, viscosity and specific heat capacity of tetralin / C₆₀ solutions and corresponding properties of the pure tetralin.

**Figure 2.** Concentration dependences of the relative difference in the density of the solutions of tetralin / C₆₀ and pure tetralin.

**Figure 3.** Concentration dependences of the absolute difference in the kinematic viscosity of the solutions of tetralin / C₆₀ and pure tetralin.

Figure 2 shows that the additives of fullerene C₆₀ lead to a slight increase in the density of tetralin. Moreover, the effect of fullerene C₆₀ is stronger at the low temperatures.

It should be noted that the additives of fullerene C₆₀ to the base fluids in contrast to other nanoparticles lead to very slight decrease in the viscosity of tetralin. This conclusion has great practical importance.
since it confirms the feasibility of using fullerene C\textsubscript{60} additives in the heat transfer agents to reduce the energy consumption by circulation pumps. The absolute effect of a decrease in viscosity of tetralin associated with the fullerene additives decreases with increasing temperature (see figure 3).

Figure 4 shows that the additives of fullerene C\textsubscript{60} contribute to decrease in the specific heat of tetralin on the boiling line (by 2.2\% at w\textsubscript{C60} =1.043 (wt.\%)). In addition, the effect of fullerene C\textsubscript{60} on the specific heat capacity of tetralin decreases with increasing temperature.

The analysis of the obtained experimental data shows that the fullerene C\textsubscript{60} additives do not significantly change the density and viscosity of tetralin. Therefore, it is not required to make changes to the few-constant equations (3), (4), and (7) that are widely used to fit the experimental data. Only constants of mentioned equations slightly change while maintaining the quality of fitting the experimental data.

Thus, the obtained experimental data on the density, viscosity and specific heat capacity of tetralin / C\textsubscript{60} solutions allow us to make several general conclusions:

- all studies of the density, viscosity and specific heat capacity were performed in the range of parameters of the existence of molecular solutions;
- the effect of small additives (up to 1.0 (wt.\%)) of fullerene C\textsubscript{60} on the tetralin thermophysical properties is small that indicates a weak nature of the intermolecular interaction between the components of solutions;
- the temperature dependences for the density, viscosity and specific heat capacity of solutions at w\textsubscript{C60}=const and pure tetralin can be fitted by similar equations, that indicates to their similar thermodynamic behavior;
- the additives of fullerene C\textsubscript{60} have very little effect on the value of pseudocritical temperature of the tetralin / C\textsubscript{60} solutions.

Unfortunately, there are any few-constant correlations in the literature can be found for predicting the specific isobaric heat capacity of both pure liquids and solutions of aromatic hydrocarbons with C\textsubscript{60} fullerene in a wide temperature range. To solve this problem, we propose to use the method for predicting the thermophysical properties of the substances on the boiling line, that is based on the application of the basic principles of scaling [7, 12]. In accordance with this method, the specific heat capacity of various pure substances and aromatic hydrocarbon / C\textsubscript{60} solutions on the boiling line can be described by equation in the following form

\[ c_p = A \cdot t^\gamma \psi(t), \]  \hspace{1cm} (9)

where \( A \) is a coefficient, which value depends on the thermodynamic properties of the substance; \( \gamma \) is a critical index having a universal value for various substances, \( \gamma=1.24 \) [13]; \( \psi(t) \) is a crossover function [12] universal for non-associated substances versus the reduced temperature \( t = 1 - T/T_c \).

However, aromatic hydrocarbons and their solutions with fullerene have a number of specificities. As indicated in [14, 15], in connection with decisive role of a benzene ring in a liquid phase of aromatic hydrocarbons and fullerene-containing solutions, supramolecular structures that affect the thermophysical properties of the substances can be formed. For this reason, there are no universal correlations in the literature for predicting the specific heat capacity on the boiling line for hydrocarbons [10], especially at the temperatures close to the melting point. This fact complicates the study of the effects of fullerene C\textsubscript{60} additives of on the specific heat capacity of tetralin. In order to clarify the effect of fullerene on the specific heat capacity of tetralin at the low temperatures, the crossover function \( \psi(t) \) should be adapted to the structural specificities of various aromatic hydrocarbons. Therefore, the numerical values of the crossover function for the tetralin / C\textsubscript{60} solutions were obtained by processing the obtained experimental data and tabular reference data on the isobaric specific heat capacity on the boiling line for the tetralin [16]

\[ \psi(t) = \frac{1 + 25.72 \cdot t + 8.068 \cdot t^2 - 47.32 \cdot t^3}{1 + 9.12 \cdot t - 21.66 \cdot t^2 + 11.03 \cdot t^3}. \]  \hspace{1cm} (10)

In the proposed correlation (10), there is only one constant \( A \) and its value is determined by limited
experimental data on the specific heat capacity of tetralin / C_{60} solutions on the boiling line. The performed analysis shows that the deviations in the reduced temperature range 0.10 ≤ \( t \) ≤ 0.60 between the obtained experimental data and the data given in [16] do not exceed the expanded uncertainty of the change in specific heat capacity (see figure 5).

The performed analysis also shows that the proposed correlation (9) can be used to predict the specific heat capacity of aromatic hydrocarbons in the reduced temperature range 0.10 ≤ \( t \) ≤ 0.55 using limited experimental data. At the reduced temperatures \( t \geq 0.55 \), structural changes that are individual for each aromatic hydrocarbon begin to appear, which affect the temperature dependence of the specific heat capacity (see figure 5). Moreover, the additives of fullerene C_{60} enhance this effect, that is consistent with the discovered effects for other thermophysical properties of fullerene-containing solutions [14, 15].

5. Conclusions
The paper presents the results of the study of fullerene C_{60} additives on the density, viscosity and specific heat capacity of tetralin on the boiling line. It is shown that the additives of fullerene C_{60} contribute to an increase in the density, viscosity and a decrease in the specific heat capacity of tetralin. We concluded that the tetralin/C_{60} solutions can be considered as the thermodynamically similar systems in the reduced temperature range 0.10 ≤ \( t \) ≤ 0.55. In contrast, in the temperature range close to the triple point (0.55 ≤ \( t \) ≤ 0.67), the additives of fullerene C_{60} enhance the formation of supramolecular structures, that complicates development of models for predicting the specific heat capacity of fullerene-containing solutions.

6. References
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Figure 4. Concentration dependence of the relative difference in heat capacity of tetralin / C_{60} solutions and pure tetralin in a liquid state.

Figure 5. Deviations of the obtained experimental data and data on the specific heat capacity on the boiling line given in [16] from those calculated by the equations (9) and (10).
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