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## **Effect of fullerene C<sub>60</sub> admixture in paraffin wax on the refractive index and phase transition temperatures**

*The paraffin wax (PW) utilized as a phase change material is promising for thermal energy storage systems. However, the application of this material is limited by its low thermal conductivity. The fullerene C<sub>60</sub> adding in PW can help to eliminate this problem. Therefore, the system PW/C<sub>60</sub> is promising for studying its properties.*

*The results of an experimental study of the refractive index of solutions of fullerene C<sub>60</sub> in PW of 52...54 °C melting point at the ranges of C<sub>60</sub> content of 0...0.052 wt. % and temperatures of 41...65 °C are presented in the study. The complex character of the concentration dependence of the refractive index on isotherms for the studied thermodynamic systems has been registered both in liquid and solid phases. Data on the effect of the C<sub>60</sub> content in PW on the temperatures of the start and finish of its phase transition is presented. At C<sub>60</sub> content in PW of 0...0.01 wt. % the temperatures of the start and finish of the phase transition decreased, at C<sub>60</sub> content of 0.01...0.04 wt. % they increased more than the pure PW temperatures and at C<sub>60</sub> content more than 0.04 wt. % they decreased again.*

*The obtained effects of a decrease and increase in the refractive index on the isotherms and temperatures of start and finish of PW crystallization can be explained by structural transformations in PW caused by C<sub>60</sub> presence. In the authors' opinion, the reason for the extreme behavior of concentration dependence of the refractive index of objects of study is the effect of C<sub>60</sub> on the density fluctuations and the quasi-crystalline structure of the liquid and solid phases. These structural transformations in PW cause a similar change in the concentration dependencies of the temperatures of the start and finish of the phase transition of objects of study.*

**Keywords:** paraffin wax (PW); fullerene C<sub>60</sub>; solution; refractive index; phase transition

**1. Introduction.** The paraffin wax (PW) utilized as phase change material (PCM) is very promising for thermal energy storage systems. These materials have a wide range of fusion temperatures and are appropriate for medium-temperature thermal energy storage applications [1, 2, 3]. However, the application of PW as PCM is limited by low thermal conductivity.

The fullerene C<sub>60</sub> adding in PW can help to eliminate this problem [2, 3]. The advantage of fullerene C<sub>60</sub> is that form a time-stable molecular solution with PW [4]. However, nowadays there are very few papers devoted to studying the PCM containing fullerene. In [2] the thermal conductivity enhancement of composite PW/C<sub>60</sub> vs. pure PW was shown. The expediency of adding the fullerene C<sub>60</sub> in PCM (binary carbonate eutectic salts) was studied in [5], however, the thermal conductivity enhancement was not recorded. Fullerene has been chosen as nanoadditives into poly(ethylene oxide), and obtained by melt-solidification method composite was investigated for thermal energy storage applications in [6]. The higher heat of melting in comparison to theoretical values has been observed for the blend with fullerene. Al-

so, it has been found that for the crystallization of samples, the incorporation of fullerene lowers the activation energy of nucleation. Therefore, further study of the properties of PW/C<sub>60</sub> solutions for use as PCM is currently important.

Within the comprehensive studies of the thermophysical properties of composite PCMs, the use of simple methods of experimental study of the nanoparticles' effect on the phase transition parameters of these materials is of interest. Conventional methods for studying the phase transitions of n-alkanes are adiabatic and differential scanning calorimetry [3, 6]. In addition, optical methods are often applied to studying the parameters of phase transitions of various substances due to their simplicity and precision [7, 8, 9, 10]. The temperatures of phase transitions (melting, crystallization, rotator phases) were determined for a number of individual n-alkanes from C<sub>19</sub>H<sub>40</sub> to C<sub>28</sub>H<sub>58</sub> by the optical method based on dynamic light scattering [9]. However, alkanes were studied as an emulsion in water [9]. In the authors' opinion, it is practical to use the refractometry method to determine the phase transition temperatures, since it provides the high accuracy of the refractive index measurement and allows to register of the structural transformations in the studying samples [7, 8, 10].

It is known that the temperature dependence of the refractive index  $n_D(t)$  exhibits a discontinuity (an abrupt change in  $n_D$ ) or a break (an abrupt change in  $dn_D/dt$ ) at the phase transition point for pure substances. An abrupt change in  $n_D(t)$  dependence is typical for the melting point of a pure substance, and a break in the  $n_D(t)$  dependence is observed during second-order phase transitions [7]. For n-alkanes (components of industrial PW) a considerable “jump” in  $n_D$  during the phase transition is typical [8]. This circumstance makes refractometry a sufficiently accurate technique for studying the phase transition temperatures in this class of substances.

The promise of the method for determining the phase transition temperatures by the refractive index temperature dependence is confirmed by the presence of recent studies that propose devices and methods for the express determination of phase transition temperatures for various substances [10]. A single-mode-no-core-single-mode (SNS) fiber optical sensor for the detection of solid-liquid and liquid-solid phase changes in n-octadecane is proposed in [10]. A large discontinuous change of the n-octadecane's refractive index during its phase transition leads to the corresponding step-like change in the transmitted optical power that can reliably indicate the phase change of the sample in the vicinity of the sensor.

The purpose of the present paper is to study the effect of the fullerene C<sub>60</sub> in industrial PW on the refractive index and phase transition temperatures by applying the refractometry method.

## 2. Experiments.

**2.1 Object of study.** The following materials have been used to prepare composite PCMs:

- paraffin wax (PW) (produced in Germany, industrial grade T-3, melting temperature 53.5 °C according to the supplier);
- fullerene C<sub>60</sub> (purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd., China, CAS# 99685-96-8), purity 0.995 kg·kg<sup>-1</sup>).

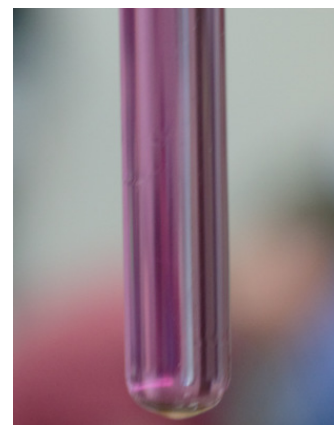
The first step of the composite PCMs preparation containing  $C_{60}$  consists of  $C_{60}$  mixing in molten PW and mechanical stirring at about  $55 \pm 5$  °C.

During the second step, the composite PCM containing  $C_{60}$  was kept for 15 days in the liquid phase at a temperature of about 60 °C in an air thermostat. This is necessary because it takes considerable time to reach the saturation equilibrium, from several hours to several days [4]. The obtained solution has been founded as supersaturated because of the presence of the undissolved crystals of fullerene  $C_{60}$  in form of a precipitate. The precipitate with crystals of  $C_{60}$

was carefully removed after PW/ $C_{60}$  crystallization. The removed PW with  $C_{60}$  precipitate was washed repeatedly by n-pentane to remove PW ( $C_{60}$  has very low solubility in n-pentane  $0.005 \text{ mg} \cdot \text{ml}^{-1}$  at 20 °C [11]) and filtered through a paper filter. The difference in mass of the dry filter with  $C_{60}$  crystals and the filter before the experiment allowed us to obtain the mass of  $C_{60}$  that was not dissolved in PW. The saturation mass fractions of  $C_{60}$  in PW at 60...65 °C is  $0.000746 \text{ g} \cdot \text{g}^{-1}$  – Fig. 1.

Composite PCM samples for further studies were obtained by diluting the saturated solution of PW/ $C_{60}$  with pure PW. The required quantity of components was measured using the Model GR 300 electronic balance with an instrument error of 0.5 mg. The  $C_{60}$  mass fraction uncertainties were evaluated as 1.0 %.

The list of samples that were used for the refractive index measurement is given in Table. 1. The image of PW samples with various content of  $C_{60}$  is shown in Fig. 2.



**Fig. 1** – Image of saturation solution of  $C_{60}$  in PW at 60 °C (mass fraction  $C_{60}$  is  $0.000746 \text{ g} \cdot \text{g}^{-1}$ )

**Table 1.** Objects of study

$C_{60}$ mass fraction, $\text{g} \cdot \text{g}^{-1}$	Shown in figures and text	$C_{60}$ mass fraction, $\text{g} \cdot \text{g}^{-1}$	Shown in figures and text
0	PW	0.000247	PW/ $C_{60}$ 0.024
0.000060	PW/ $C_{60}$ 0.006	0.000320	PW/ $C_{60}$ 0.032
0.000124	PW/ $C_{60}$ 0.012	0.000400	PW/ $C_{60}$ 0.040
0.000150	PW/ $C_{60}$ 0.015	0.000460	PW/ $C_{60}$ 0.046
0.000200	PW/ $C_{60}$ 0.020	0.000524	PW/ $C_{60}$ 0.052



**Fig. 2.** Image of the several samples in form pellet (from left to right): PW, PW/ $C_{60}$  0.006, PW/ $C_{60}$  0.012, PW/ $C_{60}$  0.020, PW/ $C_{60}$  0.024, PW/ $C_{60}$  0.052.

**2.2 Experiment technique.** An ИРФ-454Б Abbe type refractometer was used in the study. The index of refraction, relative to the air, at a wavelength of 589 nm (sodium D line) was measured. It was revealed in [12, 13] that fullerene C<sub>60</sub> in solutions of tetralin and o-xylene at low content does not absorb light of 589 nm wavelength. Convergence of readings of the refractive index is no more than  $\pm 5 \cdot 10^{-4}$ . A circulation thermostat was used to maintain a constant temperature during the refractive index measuring. The water thermostat was equipped with automatic temperature control. Temperature deviations in the thermostat from the set value did not exceed  $\pm 0.02$  °C. The uncertainty of measured temperature in the temperature-controlled part of the refractometer did not exceed 0.05 °C.

PW is a multicomponent solution, thus, after the crystallization of molten PW, the compositions of the solid sample on the surface and in the volume may differ slightly. This effect is caused by different crystallization temperatures of the PW components and thermal diffusion processes. The previously performed experimental analysis revealed that the refractive index of the samples taken in the solid state from different parts of large-volume objects of study can vary within 0.001. To eliminate the methodological error, the samples for measurements were taken from the liquid phase of the object of study, and the refractive index was measured from a higher temperature to a lower one.

**3. Results.** The measured values of the refractive index of the objects of study are presented in Fig. 3. Additionally measured values of the refractive index and the temperatures of the start and finish of the crystallization are presented in Table A.1 of the Appendix.

The data obtained reveal that the effects of small amounts of fullerene C<sub>60</sub> in PW on the refractive index variation are insignificant in absolute value. Therefore, it is advisable to analyze the concentration dependence  $n_D = f(w)$  at  $T = const$  after the experimental data fitting to reduce the influence of the random component of uncertainty.

The obtained experimental data were fitted by Eq. (1). The coefficients of Eq. (1) and its range of application are given in Table 2.

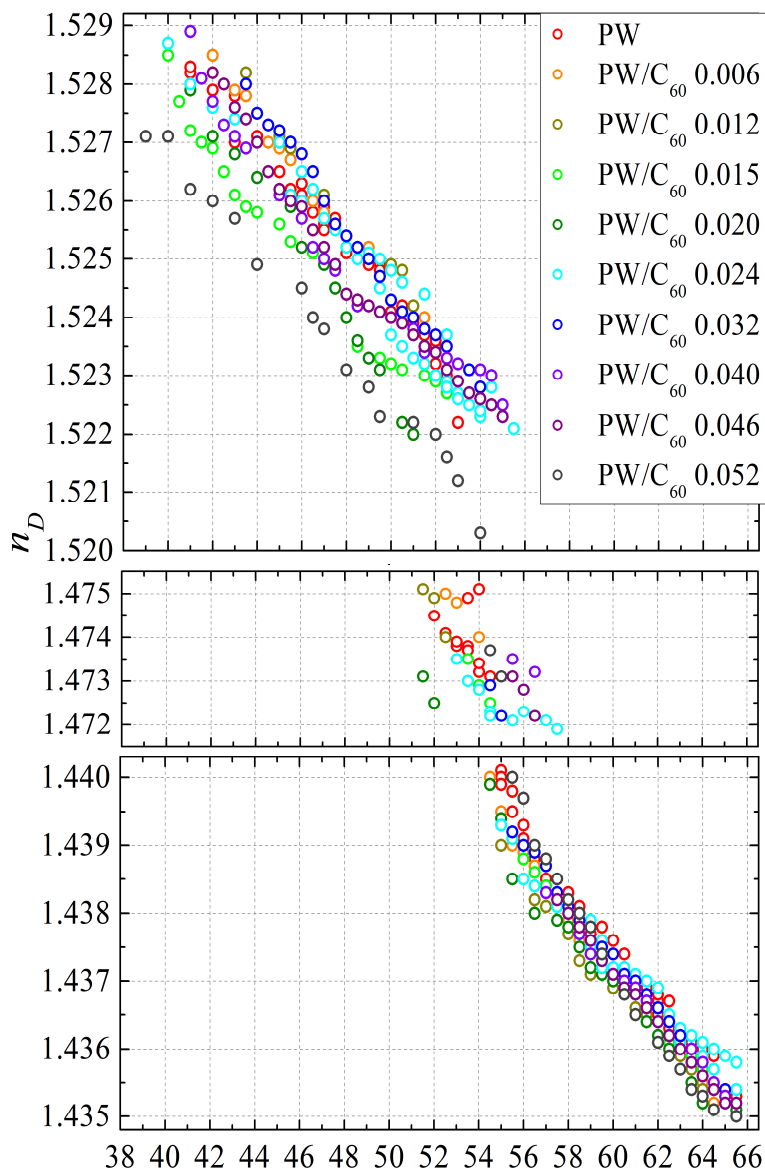
$$n_D = a + b \cdot w + c \cdot w^2 + d \cdot w^3 + e \cdot t, \quad (1)$$

where  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are the fitting coefficients;  $w$  is the mass fraction of the C<sub>60</sub>, % wt.;  $t$  is temperature, °C.

Deviations of experimental data from fitting ones are presented in Fig. 4.

The performed analysis reveals that the expanded uncertainty in measuring the refractive index of PW/C<sub>60</sub> samples did not exceed  $5.52 \cdot 10^{-4}$  for liquid phase and  $6.57 \cdot 10^{-4}$  for solid phase.

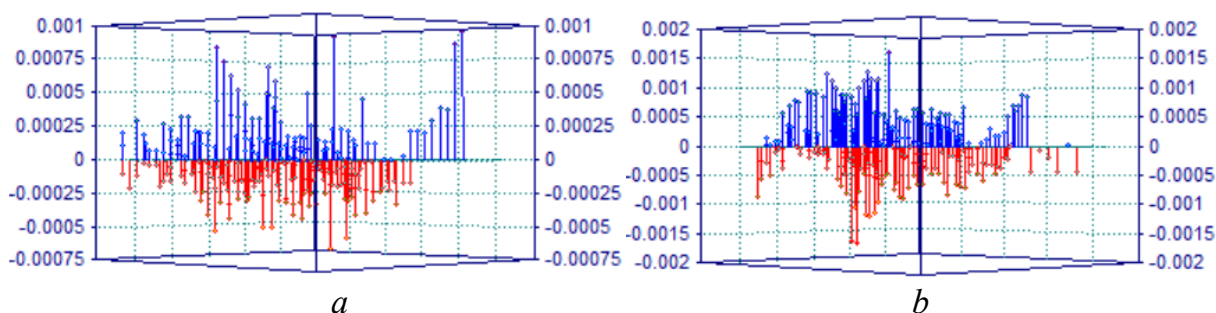
**4. Discussion.** As follows from the given in Fig. 3 information, the temperature dependencies of the refractive index of composite PCMs PW/C<sub>60</sub> represent a series of almost equidistant straight lines. Curvetting of the linear dependencies of the refractive index  $n_D(t)$  in the solid phase is observed only at temperatures below 44°C. Since industrial PW is a multi-component mixture of high molecular alkanes (from C<sub>19</sub> and



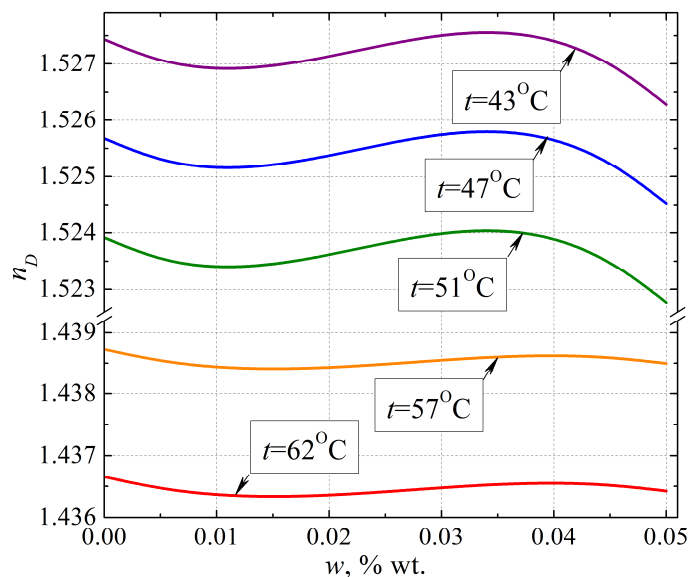
**Fig. 3.** Temperature dependence of the refractive index for objects of study

**Table 2** Fitting coefficients of Eq. (1)

Parameters	Liquid phase, temperature range 54...65 °C	Solid phase, temperature range 41...52 °C
Coefficients of determination $R^2$	0.969	0.928
Fitting standard error $\sigma$	0.000234	0.000456
$a$	1.46238	1.54634
$b$	-0.050419	-0.114336
$c$	2.33985	7.03193
$d$	-28.4598	-104.0962
$e$	-0.00041492	-0.00043969



**Fig 4.** Deviations of experimental data on the refractive index from fitting ones: a – liquid phase, b – solid phase



**Fig 5.** Concentration dependences of the refractive index in the liquid (57...62 °C) and solid (43...51 °C) phases corresponding to various isotherms

above), this curvature reflects the effects of structural transformations of some components in the solid phase.

During slow PW cooling with achieving the liquid-solid phase transition temperatures, a second total internal reflection boundary was observed at refractometry. In the authors' opinion, its presence is explained by the appearance of a new phase (Fig. 3). There are reasons to suppose [7] that under conditions of a low rate of formation of crystallization centers in PW and a strong increase in viscosity of PW the glassy state of the substance can form. The data obtained reveal that the refractive index of this phase differs significantly from the refractive index of PW in the liquid and solid crystalline states - Fig. 3. PW in the glassy state is in equilibrium with the solid phase formed during cooling. With a further decrease in temperature, the glassy state transforms into a solid state.

Fig. 5 presents the concentration dependences of the refractive index corresponding to various isotherms in the liquid and solid phases.

The analysis of the results revealed the existence of various regions with two extremes on the concentration dependences of the refractive index of the system  $PW/C_{60}n_D(w)$  at  $T=const$ . The minimum points on the dependencies  $n_D(w)$  have its confirmation with the previously obtained data for other systems [13-20].



Obviously, the complex behavior of the concentration dependencies of the refractive index of the PW/C<sub>60</sub> liquid and solid phases should have a thermodynamic substantiation. Since the thermophysical properties of substances and the refractive index are related [7], the presence of extrema should also manifest itself in the concentration dependencies of other thermophysical properties.

Up to now a lot of studies devoted to investigating the effect of fullerene on the thermophysical properties of liquids were published [4, 11, 13-20]. However, the principles of thermodynamic modeling of the nanofluids properties, including properties of solutions of PW/C<sub>60</sub> (the molecule C<sub>60</sub> in the solution can be considered both a nanoparticle and a large molecule [4]), remain developed insufficiently [13, 15, 21, 22]. In the opinion of some authors [18–22], the current situation is caused by the absence of an approach for the correct evaluation of the nanoparticles' effect on structural changes in the base fluids. It should be emphasized, that mentioned above concerns not only the formation of an interfacial phase around nanoparticles in a nanofluid but also structural changes in the base fluid at the distance from the nanoparticles.

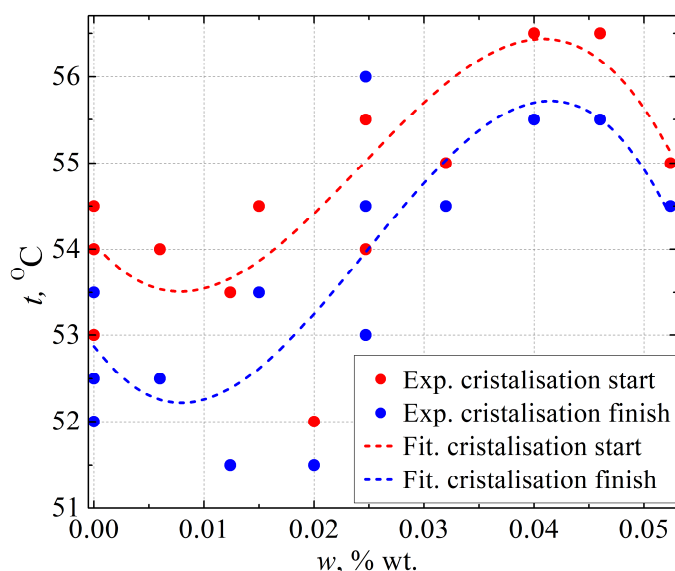
According to the mentioned, the study of the properties of fullerene solutions in hydrocarbons is of considerable interest. The interfacial layer of base liquid molecules around C<sub>60</sub> molecules is absent in these solutions. At the same time, fullerene C<sub>60</sub> solutions exhibit unusual optical, thermodynamic, kinetic, and other properties [4, 11, 13-20]: complex temperature dependence of the solubility of fullerenes in some solvents was revealed in [4, 11, 16], non-linear nature of the change in some thermophysical properties with concentration at low content of fullerene in solutions was revealed in [13-15, 17-20].

There are several hypotheses of anomalous variation in the base liquids' properties with the presence of fullerene in low content. Thus, the authors of the study [17] assume the presence of two shells around fullerene molecule in solution, first a "loose" lyophobic one, second a lyophilic one (the dense layer of base liquid).

The mentioned features of the fullerene C<sub>60</sub> behavior in solutions are explained by the recently predicted theoretically and discovered experimentally phenomenon of the formation of structural anomalies in solutions [17-20]. The dissolution of fullerene C<sub>60</sub> in aromatic solvents is typically followed by heat release and entropy decrease, which indicates structural transformations in the liquid phase of the solvent.

The most comprehensive explanation of the described phenomena is given in the studies of Ginzburg with coauthors [17-19], where the hypothesis about the appearance of regions with "zero" density in the liquid phase of aromatic hydrocarbons during the fullerene dissolving is formulated. The model of fullerene C<sub>60</sub> solutions in aromatic hydrocarbons assumes the formation of a shell with zero density around C<sub>60</sub> molecules [17]. The volume of this shell in the solution cannot be filled with liquid, since the shell's size is smaller than the size of liquid molecules. The formation of this volume by adding a low amount of fullerene C<sub>60</sub> can contribute to a decrease in the density of aromatic hydrocarbons.

A new thermodynamic hypothesis that explained the causes of fullerene C<sub>60</sub> admixtures' effect on the variation of thermophysical properties of aromatic hydrocarbons was proposed in studies [13-15]. According to the hypothesis, a low amount of



**Fig 6.** Concentration dependencies of the temperatures of the start and finish of phase transition of the PW/C<sub>60</sub>

fullerene admixtures C<sub>60</sub> contribute to an anomalous variation in fluctuations of density and volume, as well as variation in the activation energy of aromatic hydrocarbon molecules. As a result, the saturated vapor pressure, density, and viscosity of the liquid significantly change. The obtained data on the refractive index of the liquid phase of composite PCM PW/C<sub>60</sub> allow us to state that the hypothesis on the effect of fullerene admixtures on fluctuations of the thermodynamic functions is also valid for high-molecular n-alkanes.

This conclusion is confirmed by the concentration dependencies of the refractive index - Fig. 5. The refractive index values are related to the density by the Lorentz-Lorenz equation. Therefore, the decreasing refractive index in the range of fullerene concentrations of 0...0.01 wt. % is concerned with increasing the density fluctuations [13]. According mentioned above, the obtained data on the refractive index of PW/C<sub>60</sub> is thermodynamically justified. The increasing refractive index in the concentration range of 0.01...0.035 is probably concerned with the destruction of the long-range order between the molecules of the PW components (clusters), which is typical for liquids with parameters close to the triple point [23].

Refractive index values obtained in the temperature range of phase transition allow us to accurately determine the temperatures of the start and finish of melting for the PW/C<sub>60</sub>. The studying breaks of the dependencies of  $n_D(t)$  is an effective method to register the phase transformations in the objects of study. The obtained concentration dependencies of the temperatures of the start and finish of the phase transition are shown in Fig. 6.

An analysis of data presented in Fig.6 reveals that fullerene C<sub>60</sub> admixture changes the temperatures of the phase transition of the objects of study. Repeated experiments state that the melting points of the same PW/C<sub>60</sub> sample can vary within 0.5...1 °C. This effect has a random character and is typical for systems with abroken metastable state (the supercooled liquid phase transforms into a solid phase). The concentration dependence of the start and finish of the phase transition is complex. At C<sub>60</sub> content in PW of 0...0.01 wt. % the temperatures of the start and finish of the



phase transition decreased, at  $C_{60}$  content of 0.01...0.04 wt. % they increased more than the pure PW temperatures and at  $C_{60}$  content more than 0.04 wt. % they decreased again. It should be noted that the concentration dependencies of the phase transition temperatures and concentration dependencies of the refractive index are similar in shape and location of the extrema points – Figs. 5-6.

**Conclusion.** The purpose of the paper was to study the effect of the fullerene  $C_{60}$  in industrial PW on the refractive index and phase transition temperatures by applying the refractometry method.

The values of the refractive index of solutions of fullerene  $C_{60}$  in PW of 52...54 °C melting point at the ranges of  $C_{60}$  content of 0...0.052 wt. % and temperatures of 41...65 °C were obtained. The expanded uncertainty of the experimental data did not exceed  $5.52 \cdot 10^{-4}$  for liquid phase and  $6.57 \cdot 10^{-4}$  for solid phase. The complex character of the concentration dependence of the refractive index on isotherms for system PW/ $C_{60}$  has been registered both in liquid and solid phases. Data on the effect of the  $C_{60}$  content in PW on the temperatures of the start and finish of its phase transition was obtained. At  $C_{60}$  content in PW of 0...0.01 wt. % the temperatures of the start and finish of the phase transition decreased, at  $C_{60}$  content of 0.01...0.04 wt. % they increased more than the pure PW temperatures and at  $C_{60}$  content more than 0.04 wt. % they decreased again. The obtained effects of a decrease and increase in the refractive index on the isotherms and temperatures of start and finish of PW crystallization can be explained by structural transformations in PW caused by  $C_{60}$  presence. In the authors' opinion, the reason for the extreme behavior of concentration dependence of the refractive index of objects of study is the effect of  $C_{60}$  on the density fluctuations and the quasi-crystalline structure of the liquid and solid phases. These structural transformations in PW cause a similar change in the concentration dependencies of the temperatures of the start and finish of the phase transition of objects of study.

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### References:

1. Grosu Y., Zhao Y., Giacomello A., Meloni S., Dauvergne J. L., Nikulin A., ...& Faik A. Hierarchical macro-nanoporous metals for leakage-free high-thermal conductivity shape-stabilized phase change materials. *Applied Energy*. 2020. Vol. 269. 115088. <https://doi.org/10.1016/j.apenergy.2020.115088>
2. Khliyeva O. Ya., Zhelezny V. P., Nikulin A. G., Lapardin M., Ivchenko D. O., Palomo del Barrio E. Paraffin wax enhanced with carbon nanostructures as phase change materials: preparation and thermal conductivity measurement. *2021 IEEE 11th International Conference on "Nanomaterials: Applications & Properties" (NAP-2021)*. Odesa, Ukraine, Sept. 5-11, 2021. <https://doi.org/10.1109/NAP51885.2021.9568522>
3. Hlek Ya., Khliyeva O., Ivchenko D., Lapardin N., Khalak V., Zhelezny V. Express method of experimental study of carbon nanostructures effect on paraffin wax caloric properties, *Nanosystems, Nanomaterials, Nanotechnologies*, 2022, Vol. 20 (3), *in press*.

4. Mchedlov-Petrosyan N. O. Fullerenes in Liquid Media: An Unsettling Intrusion into the Solution Chemistry. *Chem. Rev.* 2013.Vol. 113 (7). P. 5149–5193. <https://doi.org/10.1021/cr3005026>
5. Tao Y. B., Lin C. H., He Y. L. Preparation and thermal properties characterization of carbonate salt/carbon nanomaterial composite phase change material. *Energy Convers. Manage.* 2015. Vol. 97. P. 103-110. <https://doi.org/10.1016/j.enconman.2015.03.051>
6. Pielichowska K., Pielichowski K. Crystallization behaviour of PEO with carbon-based nanonucleants for thermal energy storage. *Thermochimicaacta.*2010. Vol.510(1-2). P. 173-184. <https://doi.org/10.1016/j.tca.2010.07.012>
7. Ioffe B. V. Refractometric methods in chemistry. Khimiya: Leningrad. 1983. 352 p. (in Russian)
8. Johnson J. F. Phase transformations in commercial paraffin waxes, *Industrial & Engineering Chemistry.* 1954.Vol. 46(5). P. 1046-1048. <https://doi.org/10.1021/ie50533a062>
9. Kuryakov V. N., Ivanova D. D., Tkachenko A. N., Sedenkov P. N. Determination of phase transition temperatures (melting, crystallization, rotator phases) of n-alkanes by the optical method. *IOP Conference Series: Materials Science and Engineering.* 2020. Vol. 848, N 1. <https://doi.org/10.1088/1757-899X/848/1/012044>
10. Han W., Rebow M., Lian X., Liu D., Farrell G., Wu Q., Ma Y., Semenova Y. SNS optical fiber sensor for direct detection of phase transitions in C<sub>18</sub>H<sub>38</sub> n-alkane material. *Exp. Therm. Fluid Sci.* 2019.Vol. 109. 109854. <https://doi.org/10.1016/j.expthermflusci.2019.109854>
11. Ruoff R. S., Tse D. S., Malhotra R., Lorents D. C. Solubility of fullerene (C<sub>60</sub>) in a variety of solvents. *J. Phys. Chem.* 1993. Vol. 97 (13). P. 3379–3383. <https://doi.org/10.1021/j100115a049>
12. Lamosa R. A., Motovoy I., Khliiev N., Nikulin A., ... & del Barrio Elena P. Tetralin+ fullerene C<sub>60</sub> solutions for thermal management of flat-plate photovoltaic/thermal collector. *Energy Convers. Manage.* 2021. Vol. 248. 114799. <https://doi.org/10.1016/j.enconman.2021.114799>
13. Zhelezny V. P., Khanchych K. Y., Motovoy I. V., Nikulina A. S. On the nonmonotonous behavior of the thermal properties of fullerene C<sub>60</sub>/o-xylene solutions. *J. Mol. Liq.* 2021. Vol. 338. 116629. <https://doi.org/10.1016/j.molliq.2021.116629>
14. Zhelezny V., Motovoy I., Khanchych K., Sechenyh V., Hlek Y. Temperature and concentration dependencies of the saturated vapor pressure for the solutions of nanoparticles AL<sub>2</sub>O<sub>3</sub> in isopropanol and fullerenes C<sub>60</sub> in o-xylene. *J. Mol. Liq.* 2020. Vol. 319.114362. <https://doi.org/10.1016/j.molliq.2020.114362>
15. Zhelezny V. P., Khanchych K. Y., Motovoy I. V., Nikulina A. S. Viscous behaviour of o-xylene/fullerene C<sub>60</sub> solutions. *J. Mol. Liq.*2021.Vol. 328.115416. <https://doi.org/10.1016/j.molliq.2021.115416>
16. Semenov K.N., Charykov N.A., Keskinov V.A., Piartman A.K., Blokhin A.A., Kopyrin A.A., Solubility of light fullerenes in organic solvents. *J. Chem. Eng. Data.*2010. Vol. 55(1).P. 13-36. <https://doi.org/10.1021/je900296s>
17. Ginzburg B.M., Tuichiev S., Tabarov S.K., Formation of zero density regions during the dissolving of C<sub>60</sub> and C<sub>70</sub>. *J. Macromol. Sci. Part B.*2013. Vol. 52 (6).P. 773-787. <http://doi.org/10.1080/00222348.2012.721654>
18. Ginzburg B.M., Tuichiev S., Tabarov S.K., Concentration-dependent variations in the density of C<sub>60</sub> fullerene solutions in aromatic solvents. *Tech. Phys. Lett.* 2007. Vol. 33(8).P. 639-640. <http://doi.org/10.1134/s1063785007080044>

19. Ginzburg B.M., Tuichiev S., Rashidov D., Sodikov F.H., Tabarov S.H., Shepelevskii A.A., Step-wise concentration influence of fullerenes C<sub>60</sub> and C<sub>70</sub> on the various parameters of condensed systems, *J. Macromol. Sci. Part B*.2015. Vol. 54 (5).P. 533-543. <http://dx.doi.org/10.1080/00222348.2015.1010635>
20. Amer M.S., Bennet M., Maguire J.F., A Brillouin scattering study of C<sub>60</sub>/toluene mixtures. *Chem. Phys. Lett.*2008. Vol. 457 (4-6).P. 329-331. <https://doi.org/10.1016/j.cplett.2008.04.015>
21. Michaelides E.E.S., Nanofluidics: thermodynamic and transport properties. Springer International Publishing: Switzerland. 2014. 335 p. <http://doi.org/10.1007/978-3-319-05621-0>
22. Rashidi M. M., Nazari M. A., Mahariq I., Assad M. E. H., Ali M. E., Almuzaier R., ...&Murshid N. Thermophysical properties of hybrid nanofluids and the proposed models: An updated comprehensive study. *Nanomaterials*. 2021. Vol. 11(11). 3084. <https://doi.org/10.3390/nano11113084>
23. FrenkelYa.I., Kinetic theory of liquids.Nauka: Leningrad. 1975. 592 p. (in Russian)

## Appendix

Table A.1 - Experimental data on the refractive index of solutions of fullerene C<sub>60</sub> in PW (interval of phase transition temperatures in italics,  liquid phase,  solid phase)

<i>t</i> , °C	<i>w</i> , wt.%	<i>t</i> , °C	<i>w</i> , wt.%	<i>t</i> , °C	<i>w</i> , wt.%	<i>t</i> , °C	<i>w</i> , wt.%	<i>t</i> , °C	<i>w</i> , wt.%	<i>t</i> , °C	<i>w</i> , wt.%
<b>PW</b>		63.5	1.4360	<b>52.5</b>	<b><i>1.474</i></b>	<b>PW/C<sub>60</sub> 0.024</b>		50.5	1.5235	46.5	1.5252
62.0	1.4367	63.0	1.4362	<b>52.0</b>	<b><i>1.4749</i></b>	65.5	1.4354	50.0	1.5237	46.0	1.5257
61.0	1.4369	62.5	1.4363	<b>51.5</b>	<b><i>1.4751</i></b>	64.5	1.4357	<b>PW/C<sub>60</sub> 0.024</b>		45.0	1.5261
60.0	1.4372	62.0	1.4365	51.0	1.5242	64.0	1.4359	60.0	1.4372	44.5	1.5265
59.0	1.4374	61.5	1.4369	50.5	1.5248	63.5	1.4360	59.5	1.4373	43.5	1.5269
58.0	1.4379	61.0	1.4371	50.0	1.5249	63.0	1.4361	59.0	1.4375	43.0	1.5271
57.0	1.4385	60.5	1.4372	49.5	1.525	62.0	1.4364	58.5	1.4378	42.5	1.5273
56.5	1.4388	60.0	1.4374	49.0	1.5251	61.5	1.4367	58.0	1.4380	42.0	1.5277
56.0	1.4390	59.5	1.4376	48.5	1.5252	61.0	1.4369	57.5	1.4384	41.5	1.5281
55.5	1.4400	59.0	1.4379	47.0	1.5261	60.0	1.4371	57.0	1.4385	41.0	1.5289
55.0	1.4401	58.5	1.4381	46.0	1.5268	59.5	1.4375	56.5	1.4387	<b>PW/C<sub>60</sub> 0.046</b>	
<b>54.5</b>	<b><i>1.4731</i></b>	58.0	1.4383	45.5	1.5269	59.0	1.4376	56.0	1.4388	65.5	1.4352
<b>54.0</b>	<b><i>1.4751</i></b>	57.5	1.4385	45.0	1.5271	58.5	1.4378	<b>55.5</b>	<b><i>1.4721</i></b>	65.0	1.4352
<b>53.5</b>	<b><i>1.4749</i></b>	57.0	1.4388	43.5	1.5282	58.0	1.4380	<b>55.0</b>	<b><i>1.4722</i></b>	64.5	1.4354
53.0	1.5222	56.5	1.4390	<b>PW/C<sub>60</sub> 0.015</b>		<b>57.5</b>	<b><i>1.4719</i></b>	<b>54.5</b>	<b><i>1.4723</i></b>	64.0	1.4356
52.5	1.5230	56.0	1.4391	65.5	1.4352	<b>57.0</b>	<b><i>1.4721</i></b>	54.0	1.5224	63.5	1.4358
52.0	1.5235	55.5	1.4395	65.0	1.4354	<b>56.5</b>	<b><i>1.4722</i></b>	53.5	1.5225	63.0	1.4360
51.0	1.5240	55.0	1.4399	64.5	1.4355	<b>56.0</b>	<b><i>1.4723</i></b>	53.0	1.5226	62.5	1.4362
50.5	1.5242	<b>54.5</b>	<b><i>1.4731</i></b>	64.0	1.4357	55.5	1.5221	52.5	1.5228	62.0	1.4364
50.0	1.5249	<b>54.0</b>	<b><i>1.4734</i></b>	63.5	1.4359	55.0	1.5223	52.0	1.5230	61.5	1.4366
49.0	1.5251	<b>53.5</b>	<b><i>1.4737</i></b>	63.0	1.4360	54.5	1.5228	51.5	1.5232	61.0	1.4368
47.0	1.5259	<b>53.0</b>	<b><i>1.4739</i></b>	62.5	1.4361	54.0	1.5231	51.0	1.5233	60.5	1.4369
46.0	1.5263	<b>52.5</b>	<b><i>1.4741</i></b>	62.0	1.4364	53.0	1.5232	<b>PW/C<sub>60</sub> 0.032</b>		60.0	1.4371
<b>PW</b>		52.0	1.5232	61.5	1.4367	52.5	1.5233	65.0	1.4354	59.5	1.4373
65.5	1.4353	51.5	1.5237	61.0	1.4369	51.0	1.5237	64.5	1.4355	59.0	1.4376

64.0	1.4358	50.0	1.5241	60.5	1.4370	50.0	1.5240	64.0	1.4358	58.5	1.4378
63.5	1.4360	49.5	1.5248	60.0	1.4371	49.5	1.5245	63.5	1.4360	58.0	1.4380
63.0	1.4362	49.0	1.5249	59.5	1.4373	48.5	1.5250	63.0	1.4362	57.5	1.4382
62.5	1.4365	48.5	1.5250	59.0	1.4375	48.0	1.5252	62.5	1.4364	<b>56.5</b>	<b>1.4722</b>
62.0	1.4366	48.0	1.5252	58.5	1.4378	47.0	1.5260	62.0	1.4366	<b>56</b>	<b>1.4728</b>
61.0	1.4370	47.0	1.5255	58.0	1.4380	46.5	1.5262	61.5	1.4368	<b>55.5</b>	<b>1.4731</b>
59.5	1.4373	46.5	1.5258	57.5	1.4382	46.0	1.5265	61.0	1.4370	55.0	1.5223
59.0	1.4377	46.0	1.526	57.0	1.4384	45.0	1.527	60.5	1.4371	54.5	1.5225
58.0	1.4380	45.0	1.5262	56.5	1.4386	44.0	1.5275	60.0	1.4374	54.0	1.5226
57.5	1.4383	44.0	1.527	56.0	1.4388	<b>PW/C<sub>60</sub> 0.024</b>		59.5	1.4375	53.5	1.5227
57.0	1.4385	43.0	1.5278	55.5	1.4391	65.5	1.4358	59.0	1.4378	53.0	1.5229
56.5	1.4388	42.0	1.5279	55.0	1.4401	65.0	1.4359	58.5	1.4379	52.5	1.5231
56.0	1.4390	41.0	1.5283	<b>54.5</b>	<b>1.4725</b>	64.5	1.4360	58.0	1.4381	52.0	1.5234
55.5	1.4398	<b>PW/C<sub>60</sub> 0.006</b>		<b>54.0</b>	<b>1.4729</b>	64.0	1.4361	57.5	1.4383	51.5	1.5235
55.0	1.4400	65.5	1.4351	<b>53.5</b>	<b>1.4735</b>	63.5	1.4362	57.0	1.4387	51.0	1.5237
<b>54</b>	<b>1.4732</b>	64.5	1.4352	52.5	1.5227	63.0	1.4363	56.5	1.4389	50.5	1.5239
<b>53.5</b>	<b>1.4738</b>	64.0	1.4355	52.0	1.5229	62.5	1.4365	56.0	1.4390	50.0	1.524
52.5	1.5227	63.0	1.4359	51.5	1.523	62.0	1.4369	55.5	1.4392	49.5	1.5241
52.0	1.5236	62.0	1.4362	50.5	1.5231	61.5	1.4370	<b>55.0</b>	<b>1.4722</b>	49.0	1.5242
51.0	1.5239	61.5	1.4364	50.0	1.5232	61.0	1.4371	<b>54.5</b>	<b>1.4729</b>	48.5	1.5243
50.5	1.5241	61.0	1.4368	49.5	1.5233	60.5	1.4372	54.0	1.5228	48.0	1.5244
50.0	1.5243	60.5	1.4370	48.5	1.5235	60.0	1.4374	53.5	1.5231	47.5	1.5249
49.5	1.5249	60.0	1.4371	48.0	1.524	59.5	1.4376	53.0	1.5232	47.0	1.5252
48.0	1.5252	59.0	1.4374	47.5	1.5245	59.0	1.4379	52.5	1.5235	46.5	1.5255
47.0	1.5256	58.5	1.4376	47.0	1.5249	58.5	1.4380	52.0	1.5237	46.0	1.5259
46.0	1.5261	58.0	1.4379	46.5	1.5251	58.0	1.4382	51.5	1.5238	45.5	1.526
45.0	1.5262	57.5	1.4382	46.0	1.5252	57.5	1.4385	51.0	1.524	45.0	1.5262
44.0	1.5271	57.0	1.4384	45.5	1.5253	57.0	1.4387	50.5	1.5241	44.5	1.5265
<b>PW</b>		56.5	1.4387	45.0	1.5256	56.5	1.4389	50.0	1.5243	44.0	1.527
65.5	1.4354	56.0	1.4389	44.0	1.5258	56.0	1.4390	49.5	1.5247	43.5	1.5274
64.5	1.4359	55.5	1.4390	43.5	1.5259	55.5	1.4391	49.0	1.525	43.0	1.5276
64.0	1.4360	55.0	1.4395	43.0	1.5261	55.0	1.4393	48.5	1.5252	42.5	1.528
63.5	1.4361	54.5	1.4400	42.5	1.5265	<b>54.0</b>	<b>1.4728</b>	48.0	1.5254	42.0	1.5282
63.0	1.4363	<b>54.0</b>	<b>1.474</b>	42.0	1.5269	<b>53.5</b>	<b>1.473</b>	47.5	1.5256	<b>PW/C<sub>60</sub> 0.052</b>	
62.5	1.4367	<b>53.0</b>	<b>1.4748</b>	41.5	1.527	<b>53.0</b>	<b>1.4735</b>	47.0	1.526	65.5	1.4350
62.0	1.4368	<b>52.5</b>	<b>1.475</b>	41.0	1.5272	52.5	1.5237	46.5	1.5265	64.5	1.4351
61.5	1.4370	52.0	1.5237	40.5	1.5277	51.5	1.5244	46.0	1.5268	64.0	1.4353
61.0	1.4371	51.5	1.524	40.0	1.5285	50.5	1.5246	45.5	1.527	63.5	1.4354
60.5	1.4374	51.0	1.5242	<b>PW/C<sub>60</sub> 0.020</b>		50.0	1.5248	45.0	1.5272	63.0	1.4357
60.0	1.4376	50.0	1.5248	65.5	1.4351	49.5	1.5250	44.5	1.5273	62.5	1.4359
59.5	1.4378	49.5	1.525	64.0	1.4352	49.0	1.5251	44.0	1.5275	62.0	1.4361
59.0	1.4379	49.0	1.5252	63.5	1.4355	48.5	1.5252	43.5	1.528	61.0	1.4365
58.5	1.4380	47.0	1.5258	62.5	1.4360	48.0	1.5254	<b>PW/C<sub>60</sub> 0.040</b>		60.5	1.4368
58.0	1.4382	46.5	1.526	62.0	1.4362	47.5	1.5255	65.5	1.4352	59.5	1.4374
57.5	1.4385	46.0	1.5265	61.5	1.4364	47.0	1.5257	65.0	1.4353	59.0	1.4378
57.0	1.4388	45.5	1.5267	61.0	1.4365	46.0	1.5260	64.5	1.4355	58.5	1.4380
56.5	1.4390	45.0	1.5269	60.0	1.4370	45.5	1.5261	64.0	1.4358	58.0	1.4382
56.0	1.4393	44.5	1.527	59.5	1.4371	45.0	1.5262	63.5	1.4360	57.5	1.4385
55.5	1.4395	43.5	1.5278	59.0	1.4372	44.0	1.5270	62.5	1.4362	57.0	1.4388



55.0	1.4400	43.0	1.5279	58.5	1.4375	43.0	1.5274	62.0	1.4364	56.5	1.4390
<b>53.0</b>	<b>1.4738</b>	42.0	1.5285	58.0	1.4378	42.0	1.5276	61.5	1.4367	56.0	1.4397
<b>52.5</b>	<b>1.4740</b>	<b>PW/C<sub>60</sub> 0.012</b>		57.5	1.4379	41.0	1.5280	61.0	1.4369	55.5	1.4400
<b>52.0</b>	<b>1.4745</b>	65.5	1.4351	56.5	1.4380	40.0	1.5287	60.5	1.4370	<b>55</b>	<b>1.4731</b>
51.5	1.5232	65.0	1.4352	55.5	1.4385	<b>PW/C<sub>60</sub> 0.024</b>		60.0	1.4371	<b>54.5</b>	<b>1.4737</b>
51.0	1.5238	64.0	1.4354	55.0	1.4394	60.0	1.4371	59.0	1.4374	54.0	1.5203
50.0	1.5240	63.5	1.4357	54.5	1.4399	59.5	1.4372	58.5	1.4377	53.0	1.5212
49.5	1.5248	63.0	1.4359	<b>52.0</b>	<b>1.4725</b>	59.0	1.4374	58.0	1.4380	52.5	1.5216
49.0	1.5249	62.5	1.4360	<b>51.5</b>	<b>1.4731</b>	58.5	1.4378	57.5	1.4382	52.0	1.522
48.0	1.5251	62.0	1.4362	51.0	1.522	58.0	1.4380	57.0	1.4383	51.0	1.5222
47.5	1.5257	61.5	1.4365	50.5	1.5222	57.5	1.4381	<b>56.5</b>	<b>1.4732</b>	49.5	1.5223
47.0	1.5259	61.0	1.4366	49.5	1.5231	57.0	1.4383	<b>55.5</b>	<b>1.4735</b>	49.0	1.5228
46.0	1.5261	60.5	1.4368	49.0	1.5233	56.5	1.4384	55.0	1.5225	48.0	1.5231
45.5	1.5262	60.0	1.4369	48.5	1.5236	56.0	1.4385	54.5	1.523	47.0	1.5238
45.0	1.5265	59.0	1.4371	48.0	1.524	<b>55.5</b>	<b>1.4721</b>	54.0	1.5231	46.5	1.524
43.5	1.5269	58.5	1.4373	47.5	1.5245	<b>55.0</b>	<b>1.4722</b>	53.0	1.5232	46.0	1.5245
43.0	1.5270	58.0	1.4377	47.0	1.5249	<b>54.5</b>	<b>1.4722</b>	52.5	1.5233	44.0	1.5249
42.0	1.5277	57.5	1.4379	46.0	1.5252	54.0	1.5223	51.5	1.5234	43.0	1.5257
41.0	1.5282	57.0	1.4381	45.5	1.5259	53.5	1.5225	51.0	1.5238	42.0	1.526
<b>PW</b>		56.5	1.4382	45.0	1.5261	53.0	1.5227	50.0	1.524	41.0	1.5262
65.5	1.4351	56.0	1.4385	44.0	1.5264	52.5	1.5229	49.5	1.5241	40.0	1.5271
65.0	1.4352	55.0	1.4390	43.0	1.5268	52.0	1.523	48.5	1.5242	39.0	1.5271
64.5	1.4355	<b>53.5</b>	<b>1.473</b>	42.0	1.5271	51.5	1.5232	47.5	1.5248	-	-
64.0	1.4358	<b>53.0</b>	<b>1.4735</b>	41.0	1.5279	51.0	1.5233	47.0	1.525	-	-

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### **Вплив домішок фулерену C<sub>60</sub> на значення показника заломлення та температури фазових переходів технічного парафіну**

#### **Анотація:**

*Технічний парафін, як матеріал з фазовим переходом, є перспективним для його застосування у термоакумулятивних системах. Однак його широке впровадження обмежене низькою теплопровідністю. Згладити цей недолік можна за рахунок додавання до парафіну фулерену C<sub>60</sub>. Тому система парафін/C<sub>60</sub> є перспективною для дослідження її властивостей.*

*У роботі наведено результати експериментального дослідження показника заломлення розчинів C<sub>60</sub> у технічному парафіні з температурою плавлення 52...54 °С у діапазонах концентрацій 0...0,052 мас. % C<sub>60</sub> та температур 41...65°С. Відзначено складний характер концентраційної залежності показника заломлення на ізотермах для досліджуваної термодинамічної системи як в рідкій фазі, так й в твердій. Наведено дані про вплив концентрації C<sub>60</sub> у парафіні на температури початку та кінця його фазового переходу. Показано, що в інтервалі концентрацій 0...0.01 мас. % C<sub>60</sub> в парафіні температури початку та кінця фазового переходу зменшуються, при вмісті C<sub>60</sub> 0.01...0.04 мас. % - збільшуються (перевищуючи ці показники для парафін), а з підвищенням вмісту C<sub>60</sub> більш ніж 0.04 мас. % - знову зменшуються.*

*Отримані ефекти зменшення та збільшення показника заломлення на ізотермах та температур початку та кінця кристалізації парафіну пов'язані зі структурними перетвореннями в парафіні в присутності  $C_{60}$ . На думку авторів, причиною екстремальної поведінки концентраційної залежності показника заломлення об'єктів дослідження є вплив  $C_{60}$  на величину флуктуацій густини та квазікристалічну структуру рідкої та твердої фази. Ці структурні перетворення у парафіні, у свою чергу, призводять до аналогічних змін концентраційних залежностей температур початку та кінця фазових переходів об'єктів дослідження.*

**Ключові слова:** *технічний парафін; фулерен  $C_{60}$ ; розчин; показник заломлення; фазовий перехід*