



Thermodiffusion and coupled phenomena / Thermodiffusion et phénomènes couplés

Determination of thermal diffusion coefficient of nanofluid: Fullerene–toluene

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ABSTRACT

Thermodiffusion coefficient at fullerene mass concentrations of 0.05%, 0.1%, 0.15%, and 0.2% was established for pure fullerene (C_{60}) diluted in toluene solutions. For this, the thermogravitation technique has been used in planar configuration with 4 extraction points. The determination of the concentration distribution along the column in steady state is determined by the method of analysis based on density measurements. In order to determine the thermal diffusion coefficient all thermophysical properties such as density, viscosity, thermal expansion coefficient and mass expansion coefficients were determined. All these studies coincide with the importance of the knowledge of the thermophysics and transport properties of the nanofluids to develop new applications and to optimize the existing ones.

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1. Introduction

The fullerene is one of the new materials that has attracted more interest from scientists since its discovery in 1985 by Harold Kroto et al. [1]. This material is the third allotropic form known of carbon, thus is part of the family of the graphite and diamond. However, while the graphite and diamond reticular structures are indefinitely extending, fullerenes form a molecular structure, i.e. they are discrete molecules constructed by a number of carbon atoms. Its atomic structure gives unique features, one of the most important is their high symmetry, in fact, it is the most symmetrical molecule known. Its structure consists of 60 atoms, 12 pentagons and 20 hexagons, which form a soccer ball with a diameter of 10 Å and an empty cavity inside.

The fullerene is produced naturally in small quantities by coal-fired power plants [2], lightning and has even been found in the meteorite that impacted in Allende, Mexico [3]. The most common fullerene is called C_{60} , however more fullerenes have been discovered, C_{70} , C_{540} or nanotubes. Different types of fullerenes can be observed in Fig. 1.

Since its discovery, due to its variety of properties, different applications in different areas have been attributed to it. Thus, although its molecular structure is very resistant (can withstand up to 3000 bar), the attachment of molecules is particularly weak (Van der Waals). This is why it is used as an additive in the lubricants, creating a new generation of nanofluidic lubricants [4]. At chemical level, the C_{60} is very electronegative, therefore it forms easily compounds with donor atoms. An obvious combination is the C_{60} with an alkaline metal, as it is very electropositive. Thus it is achieved through the union of potassium (K) or rubidium (Rb) superconducting molecules character [5]. Their potential in optical applications can also be shown because their properties vary with UV light exposure [6].

The fullerene capacity to dissolve in common organic solvents is the property why there have been so many studies. Due to this capacity, it is possible to create many fullerene derivatives maintaining their exceptional properties. Thus, new

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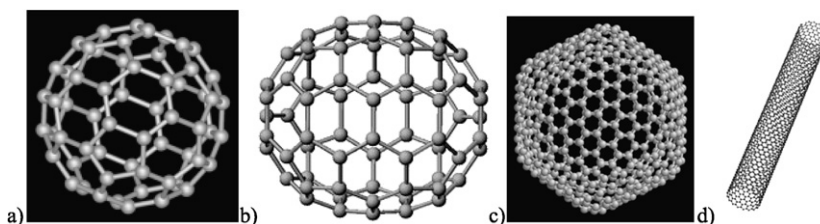


Fig. 1. Different kinds of fullerenes. a) C₆₀, b) C₇₀, c) C₅₄₀ and d) nanotube.

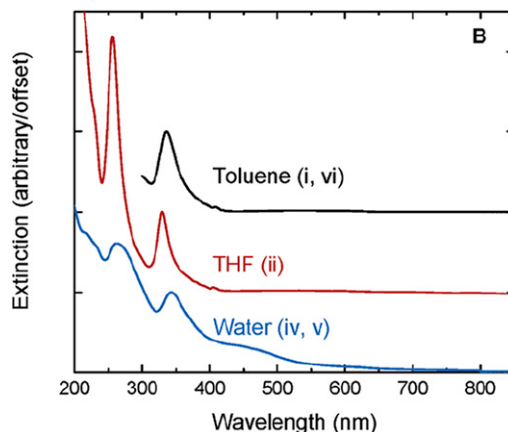


Fig. 2. Spectral analysis of C₆₀ dissolved in toluene, THF and water [13].

polymers were created with additives of C₆₀ providing their properties such as hardness and low density. Besides, through the possibility of dissolving in organic solvents, its dissolution in aqueous media has been achieved [7]. This has ensured its application in biology, arousing great interest in medical applications. Because of its size, some experiments have been carried out in order to use it as an inhibitor of the protease that causes AIDS virus (HIV) [8,9]. Moreover, its similarity in size with common drugs makes it viable as a possible drug carrier [10].

Other scientists have taken advantage of its internal cavity, and they have added up to three different atoms inside. Most of them have introduced metal atoms (metallofullerenes) or noble gases in order to use in MRI or X-ray visualization [11,12]. These applications are of great interest especially against cancer. In addition, the human body can easily tolerate fullerenes as they are composed entirely of carbon. Once they have finished their functionality, the C₆₀ is small enough to be expelled by the body. However, larger fullerenes tend to accumulate in the lung, liver and bones. Some studies have shown some harmful behaviour in the human being with this type of nanoparticles [13]. This adverse situation has its origin in the low solubility of these nanoparticles in aqueous media (approximately 1.6 mg/ml). When they are used in organic solvents such as toluene, the solubility is 2.9 mg/ml, the solution is molecular. However, in aqueous solutions, at certain concentrations of fullerene C₆₀ generates aggregates or nanocrystals [7,13]. It can be concluded that these aggregations are responsible for their toxicity. These structures and their morphology are still ambiguous and questionable, therefore it is important to carry out a study. Fig. 2 shows a spectral analysis of C₆₀ in different solvents, which affords a unique excitation around 340 nm for organic solvents; toluene and THF. This excitation corresponds to C₆₀ molecules. However, in the aqueous solution of C₆₀ spectrum, two excitations can be observed, one around 340 nm (C₆₀) and other around 490 nm corresponding to nanocrystals formed by C₆₀ molecules.

It can be concluded the strong interest of fullerene C₆₀ in medical applications. Consequently, this work has focused on the characterization of the first and second order thermophysical and transport properties of nanofluid (toluene–fullerene C₆₀) for 0.05, 0.1, 0.15 and 0.2 mass fractions concentration percentage of fullerene. In particular, it has been determined the density, dynamic viscosity, thermal diffusion coefficient and mass and thermal expansion coefficients. This study will improve the knowledge of the behaviour of these interesting nanoparticles in the presence of a temperature gradient, likewise it can optimize the potential applications related with transport phenomena in this type of nanofluid.

2. Material and method

Preparation of the samples are carry out with fullerene C₆₀ (SES Research, ≥ 99.5% purity) and toluene (Merck, purity ≥ 99.9%). Samples have been made at different mass concentrations: fullerene mass fraction percentages of 0.05, 0.1, 0.15 and 0.2. Due to the difficulties dissolving fullerene in toluene no major mass fractions mixtures were done. For these mixtures, a precision balance Gram VXi-310 of an accuracy of 0.0001 g is used. The dynamic viscosity has been determined by a

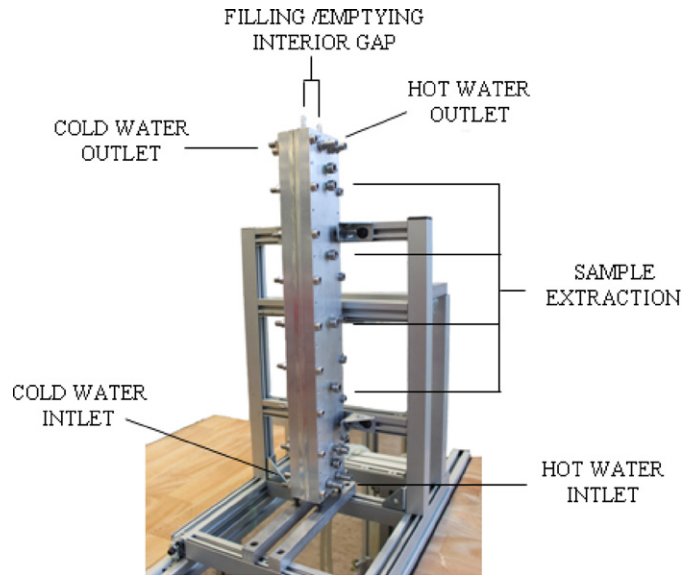


Fig. 3. Thermogravitational column configuration.

ball drop microviscosimeter Anton Paar AMVn with a viscosity accuracy of 10^{-6} Pa s and temperature stability of ± 0.01 °C. In order to determine density, thermal and mass expansion coefficients, an Anton Paar DMA 5000 vibrating quartz U-tube densimeter is used. It has a reproducibility of 1×10^{-6} g/cm³ with a temperature accuracy of 0.01 °C. Finally, for the thermal diffusion coefficient, the thermogravitational technique with 4 extraction points has been used. Due to the nanofluidic character of the mixtures, a new experimental protocol has been made, in order to avoid possible contamination in the mixtures. For this aim, we have proposed an experimental procedure that involves the systematic cleaning and calibration for each measurement made in the thermogravitational installation. This procedure avoids possible erroneous measurements due to the contamination. The validation of the proper functioning of the thermodiffusive systematic process has been carried out with toluene–hexane mixture at toluene mass fraction of 0.5167, which thermal diffusion coefficient is well defined in the literature [14,15]

3. Experimental procedure

To determine the thermodiffusion coefficient, the thermogravitational column (TC) technique is used. In this case a flat configuration with four-point sample extraction is used (Fig. 3), with a column height of 500 mm and a gap of 1 ± 0.005 mm. For more details about the experimental procedure of this technique the reader is invited to consult [16] where the procedure is fully explained.

The thermodiffusion coefficient can be determined by measuring the change in the density of samples at steady state along the column, as shown in Eq. (1) [15]:

$$D_T = -\frac{gL_x^4}{504} \frac{\alpha}{c_0(1-c_0)\beta\eta} \frac{\partial\rho}{\partial z} \quad (1)$$

where L_x is the gap between the two vertical walls of the TC, which is 1 ± 0.005 mm, c_0 is the initial mass fraction of the reference component in the initial homogeneous mixture. The thermal expansion coefficient $\alpha = -\frac{1}{\rho} \frac{\partial\rho}{\partial T}$ is determined from a calibration curve which relates density with temperature. For this purpose a mixture with the initial mass fraction at five different temperatures close to the average temperature are measured ($\Delta T = 25 \pm 1$ °C). The mass expansion coefficient $\beta = \frac{1}{\rho} \frac{\partial\rho}{\partial c}$ is determined from a calibration curve which relates mass fraction and density. In order to make the calibration, five mixtures with known concentration, close to the initial mass fraction ($c_0 \pm 0.02$) are prepared by weighing. ρ is the density of the mixture with the initial mass concentration c_0 , $\frac{\partial\rho}{\partial z}$ is the vertical density gradient along TC in steady state, g is the gravitational acceleration and η is the dynamic viscosity.

In thermogravitational columns three effects are combined: first, the horizontal thermodiffusion flow generated by the horizontally applied temperature gradient; next, the molecular diffusion flow due to the concentration difference; and finally, the convection flow due to the gravitational field and the horizontal density gradient. The thermodiffusion coefficient of a given component is positive when this component, being the heaviest one, goes toward the cold wall, giving rise to enrichment in this component at the bottom of the column, whereas the other component goes to the hot wall giving rise to enrichment in this second component at the top of the column.

Table 1Thermophysics and transport properties of toluene–fullerene C₆₀ at 25 °C.

Mass fraction concentration (%)	Density (kg/m ³)	η (Pa s) (10 ⁻³)	β	α (K ⁻¹) (10 ⁻³)	D_T (m ² /sK) (10 ⁻¹¹)
0.05	862.42	0.5576	0.621	1.079	5.435
0.1	862.65	0.5580	0.608	1.080	3.881
0.15	862.91	0.5583	0.598	1.080	3.415
0.20	863.14	0.5587	0.578	1.079	3.398

4. Experimental results

All experiments are performed at 25 °C. In order to obtain consistent results, all the measurements are conducted at least 4 times under the same working conditions and the deviation of the thermal diffusion coefficient has been below 4%. Table 1 shows the thermophysical and transport properties determined for the toluene–fullerene mixtures at different mass concentrations and at 25 °C. Density, dynamic viscosity η , mass expansion coefficient β and the thermal expansion coefficient α are represented respectively.

Fig. 4 shows the results of the density, dynamic viscosity η , mass expansion coefficient β and the thermal expansion coefficient α respectively for different mass concentrations.

Regarding the results, as the concentration of fullerene increases, both the density and the viscosity increase linearly. However, the mass expansion coefficient has an opposite trend, decreases linearly with the concentration of fullerene. On the other hand, it has been demonstrated that the thermal expansion coefficient is constant, i.e., is independent of the concentration of fullerene. Even toluene being one of the best solvents for fullerene, its solubility still remains minimal, about 2.9 mg/ml. Therefore, when using such small concentrations of solute, the variations in thermophysical properties results are minimal. Thus, the development of the mixtures must be very precise because a small variation in the mass of the solute or the solvent makes a huge change in final concentration.

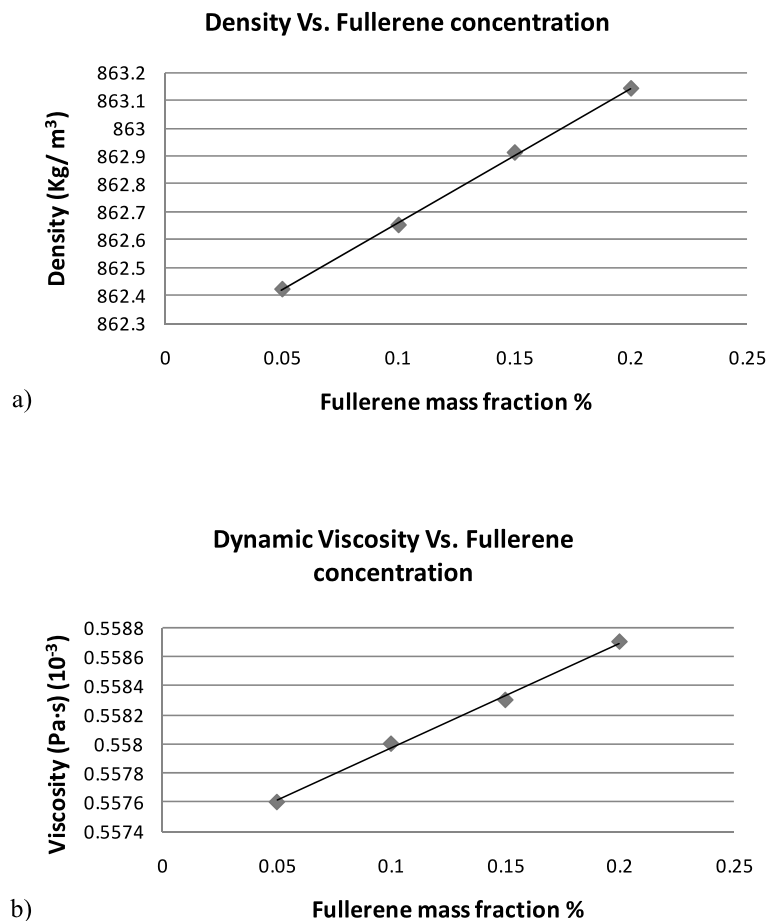


Fig. 4. a) Density vs. fullerene mass fraction. b) Dynamic viscosity vs. fullerene mass fraction. c) Mass expansion coefficient vs. fullerene mass fraction. d) Thermal expansion coefficient vs. fullerene mass fraction at 25 °C.

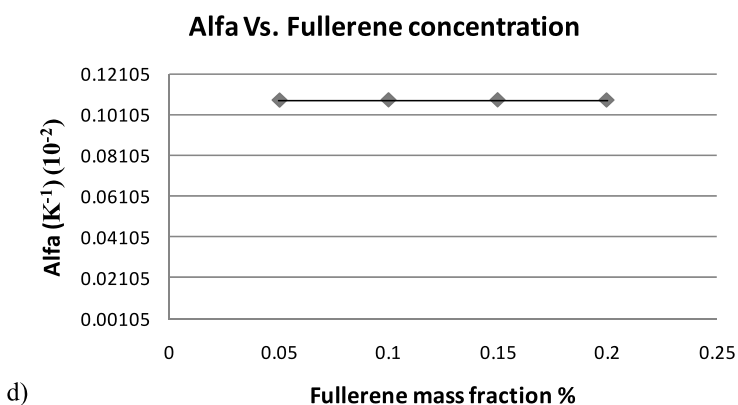
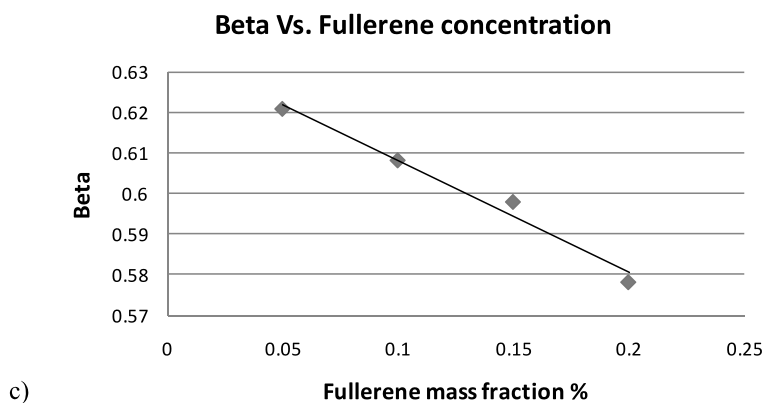


Fig. 4. (continued)

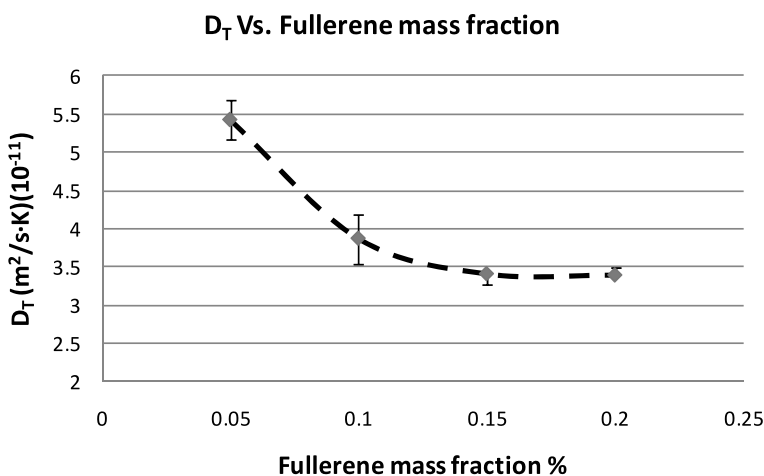


Fig. 5. Thermal diffusion coefficient vs. fullerene mass fraction at 25 °C.

After obtaining all the necessary thermophysical properties, the thermal diffusion coefficient (D_T) has been determined for different concentrations of fullerene. These results are represented in Fig. 5.

As it can be seen the thermal diffusion coefficient is at the same range as common binary liquids mixtures coefficients. In this case, the thermal diffusion coefficient decreases in a not linear way with concentration, however, this trend changes close to the solubility limit to a constant value becoming independent of the mass fraction. This behaviour was confirmed in polymers too, where D_T was found independent of molecular weight [17], i.e. the polymer chain length. Even in simple fluid

mixtures, such as alkanes, the molar mass independent thermodiffusion behaviour was demonstrated [18]. It is verified too, since D_T is positive, that these kinds of mixtures have a positive Soret effect behaviour, i.e., when a temperature gradient is applied, the heaviest component (fullerene C_{60}) goes toward the cold wall.

5. Conclusion

We have measured nanofluid (toluene–fullerene C_{60}) first and second order thermophysical and transport properties, at fullerene mass fractions percentages of 0.05, 0.1, 0.15 and 0.2. Due to the results obtained it has been observed that the behaviour of the thermophysical properties is linear in function of concentration. In addition, it was determined that the thermal expansion coefficient is constant, so, independent of the concentration of fullerene. On the other hand, it has been seen that the thermal diffusion coefficient is at the same range of common binary liquids mixtures and tends to a constant value close to the solubility limit. Thanks to these results, an improvement and an optimization of the potential applications related to the transport phenomena in nanofluids can be achieved.

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