FLOW BEHAVIOUR OF GLYCOLATED WATER SUSPENSIONS OF FUNCTIONALIZED GRAPHENE NANOPLATELETS

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ABSTRACT

The heat transfer performance of the conventional fluids used in heat exchange processes improves by dispersing nanoparticles with high thermal conductivity, as many researches have shown in the last decades. The heat transfer capability of a fluid depends on several physical properties among which the rheological behavior is very relevant, as we have previously pointed out.

In this study, different samples of nanofluids have been analyzed by using a DHR-2 rotational rheometer of TA Instruments with concentric cylinder geometry in the temperature range from (278.15 to 323.15) K. The used base fluids were two different binary mixtures of propylene glycol and water at (10:90)% and (30:70)% mass ratios. Two different mass concentrations (viz. 0.25 and 0.5 wt.%) of graphene nanoplatelets functionalized with sulfonic acid (graphenit-HW6) were dispersed in these two base fluids.

Firstly, with the goal of checking and calibrating the operation of the rheometer, the viscosity-shear stress curves for pure propylene glycol, Krytox GPL102 oil, and the two base fluids were experimentally determined. A detailed comparative study with those well-known data over the entire range of temperature was stabilized obtaining deviations in viscosity less than 3.5%. Then, the flow curves of the different nanofluid samples were studied at different temperatures to characterize their flow behavior.

INTRODUCTION

The enhancement of the heat transfer performance has raised great interest during the last century since an increment in the efficiency of thermal facilities could lead to huge savings in their initial and operational costs [1]. Once different approaches such as the use of extended surfaces or the optimization of flow conditions have been extensively investigated, many researchers focus on improving the weak thermal capabilities of most conventional working fluids. A promising way to achieve this aim is by dispersing nano-sized particles with high thermal conductivity in these conventional heat transfer fluids (HTFs). These new nanostructured materials are known as nanofluids and exhibit clear advantages regarding the dispersions of millimeter or micrometer particles such as lower pressure drops or clogging issues [2-3].

Among the different nanoadditives used to design new nanofluids in the past decade, carbon allotropes seem to be those with the most remarkable potential [4]. Within the graphite family, the exceptional mechanical, thermal and electrical properties of graphene (ideally envisaged as a single-atom-thick sheet of hexagonally arranged, sp^2-bonded carbon atoms tightly packed into a honeycomb lattice) has attracted great attention since this structure was experimentally isolated by Novoselov et al. [5]. Graphene is commercially available in the form of some-layer stacks (normally between 10-100 layers) known as graphene nanoplatelets which combine the properties of single-layer graphene as well as the possibility of being easily and cost-effectively synthesized. Nevertheless, graphene is hydrophobic and it is not possible to obtain dispersions in water for a long time [6-7]. In the case of graphene oxides (GOnPs), their basal planes and sheet edges contain different functional groups and as a consequence the material becomes hydrophilic. The drawback is that the thermal conductivity of graphene oxide is considerably lower than that of pristine graphene since the oxidation process destroys the systematically arranged conjugated structure. Through a reduction of exfoliated graphene oxide, it is possible both to restore the properties of graphene and maintain dispersibility [7].

Different works have shown that the dispersion of nanoparticles remarkably increases the thermal conductivity of conventional HTFs which may lead to improve the heat transfer performance. However, it must also be considered that the addition of nanomaterials can also alter other thermo-physical properties which, in turn, can sometimes offset the thermal conductivity enhancements. Thus, the viscosity (a fundamental property in the Reynolds number) has a strong influence on the flow regime and, consequently, on the heat transfer, for instance. Additionally, an increase in this property can lead to higher pressure drops and, therefore, higher pumping powers [8]. The Newtonian or non-Newtonian nature of the nanofluids

is also a key issue to define the flow type. In addition to study the flow behavior and assess the penalty in pressure drop, the rheological properties of nanofluids are also helpful to analyze the nanoparticle structuring within the dispersions [8-10].
The rheological properties of graphene nanofluids based on water (W) [7, 11-13] or ethylene glycol (EG) [14] have already been studied in the literature. However, up to our knowledge, no research was developed using binary mixtures of propylene glycol and water. In this study, the flow behavior of two graphene nanoplatelet nanofluid sets has been analyzed in the temperature range from (278.15 to 323.15) K by using a DHR-2 rotational rheometer (TA instruments; DE, USA) equipped with concentric cylinder geometry. The nanofluids were designed using two different (propylene glycol + water) mixtures at (10:90)% and (30:70)% mass ratios as base fluids and two mass fractions (φ= 0.0025 and φ= 0.005) of graphene nanoplatelets stabilized with sulfonic acid (graphenit-HW6).

NOMENCLATURE

AAD		Absolute Average Deviation
A, B		Adjustable parameters in equation (2)
GOnP		Graphene oxide nanoplatelet
PG		Propylene glycol
T	[K]	Temperature
η_0, *C*, T_0		Adjustable parameters of Vogel-Fulcher-Tamman (VFT) model, equation (1)
W		Water
Special characters		
η	[mPa·s]	Dynamic viscosity
φ	[-]	Graphene oxide nanoplatelet mass fraction
Subscripts		
bf		Base fluid
nf		Nanofluid
np		Nanoparticle

EXPERIMENTAL

Materials and sample preparation

Sulfonic acid-functionalized graphene nanoplatelets (graphenit-HW6) were provided by NanoInnova Technologies S.L. (Madrid, Spain, www.nanoinnova.com). The base fluids are two (propylene glycol + water) mixtures at (10:90)% and (30:70)% mass ratios. Propylene glycol was purchased from Sigma-Aldrich with a mass purity of 99.5%, while Milli-Q Grade water was produced with 18.2 MΩ·cm at 298.15 K by means of a Milli-Q 185 Plus system (Millipore Ltd, Watford, UK). Nanofluids were designed following a two-step method. Therefore, the amounts of powder and base fluid necessary to obtain the desired nanoparticle mass concentrations (0.25 and 0.5 wt.%) were first weighted in a Sartorius electronic balance model CPA225 (Sartorius AG, Germany) and then stirred at 1500 rpm for 60 minutes. Afterwards, samples were sonicated for 240 minutes by using an ultrasonic bath (Ultrasounds, JP Selecta S.A., Spain) working with a maximum sonication power of 200 W and a frequency of 20 kHz.

Experimental methods

The shear rate dependence of viscosity, the so-called flow curve, was studied at six different temperatures ranging from (278.15 to 323.15) K by means of a combined motor-transducer Discovery Hybrid Rheometer (DHR-2, TA instruments). This instrument was equipped with a coaxial cylinder geometry consisting of an external cup (diameter: 30.37 mm) and a double gap rotor (bob diameter: 27.98 mm, length: 42.17 mm, and operating gap: 5912.87 μm) which is appropriate to prevent evaporation of the sample at high temperatures. Sample temperature was controlled by using a Peltier jacket and an equilibration time of at least 20 minutes was waited before experiments in order to ensure a uniform initial temperature. Tests were performed in steady-state regime at shear rates logarithmically increasing from (0.1 to 100) s^{-1} with at least five points per decade. With the aim of checking and calibrating the operation of the rheometer, the viscosity-shear stress curves were also determined for Kryptox GPL 102 oil and pure propylene glycol over the entire temperature range. A detailed comparative between the experimental viscosities here obtained and values previously reported in the literature [10, 15-20] for these materials is presented in Figure 1.

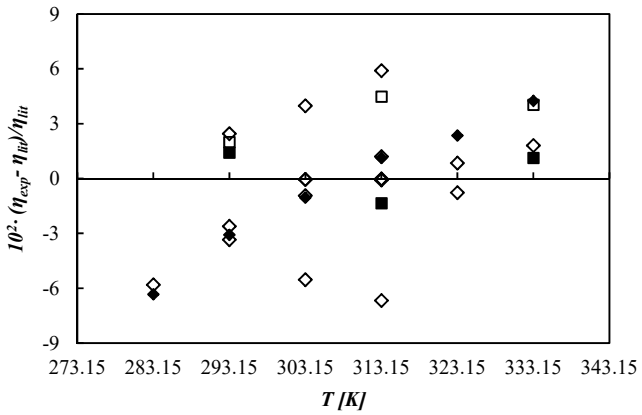

Figure 1 Comparison between experimental and literature viscosities at different temperatures for: (◆) Kryptox GLP 102 oil [16, 21], (◇) propylene glycol, PG, [10, 15, 17-18, 20], (■) PG+W mixture at (10:90)% [22] and (□) PG+W at (30:70)% [22].

The relative deviations and average absolute deviations are lower than 3%.

RESULTS AND DISCUSION

The rheological behavior of the two base fluids and the four designed nanofluids was analyzed at temperatures ranging from (278.15 to 323.15) K. As an example, Figure 2 shows viscosity vs. shear rate for the 0.25 wt.% GOnPs (PG+W at 30:70 wt.%) nanofluid at five temperatures whereas Figure 3 shows the viscosity vs. shear rate dependences for the different samples at 293.15 K.

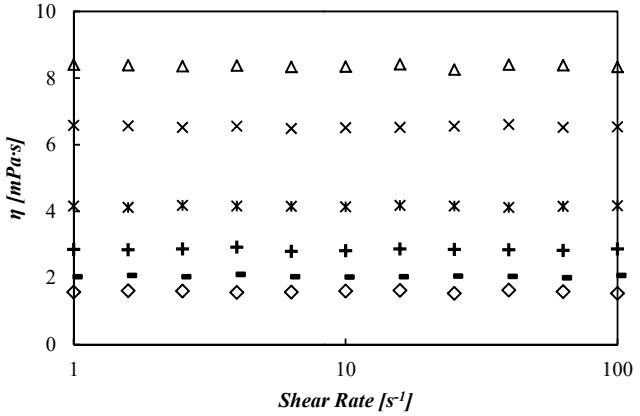

Figure 2 Flow curve for 0.25 wt.% GOnPs (PG+W at 30:70 wt.%) nanofluid at (△) 278.15 K, (×) 283.15 K, (∗) 293.15 K, (+) 303.15 K, (-) 313.15 K and (◇) 323.15 K.

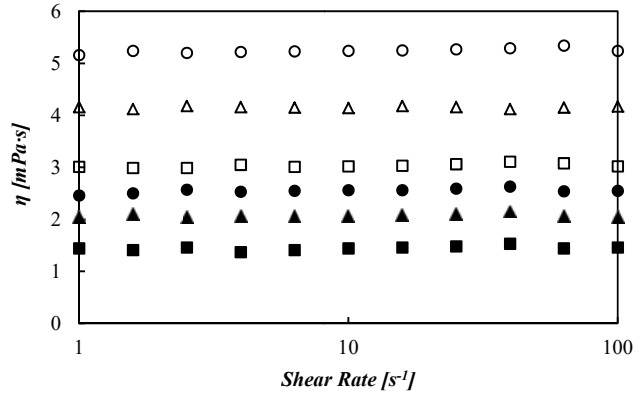

Figure 3 Flow curve at 293.15 K for: (■,▲,●) (PG+W at 10:90 wt.%) and (□,△,○) (PG+W at 30:70 wt.%) nanofluids sets. (■,□) Base fluid, 0 wt.%, (▲,△) 0.25% and (●,○) 0.5% mass concentrations/wt%.

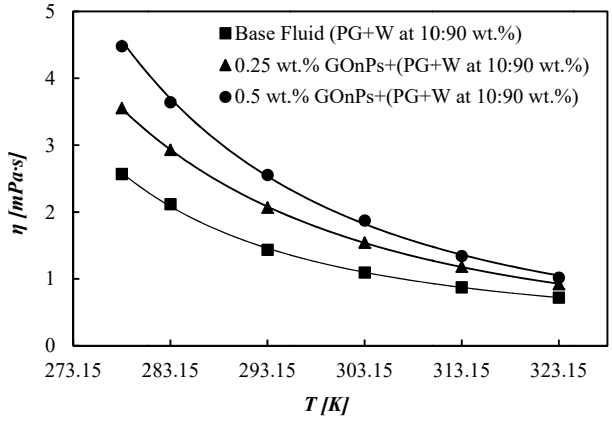

Figure 4 Temperature dependence of dynamic viscosity of GOnPs in (PG+W) at (10:90) wt.%. (—) VFT equation.

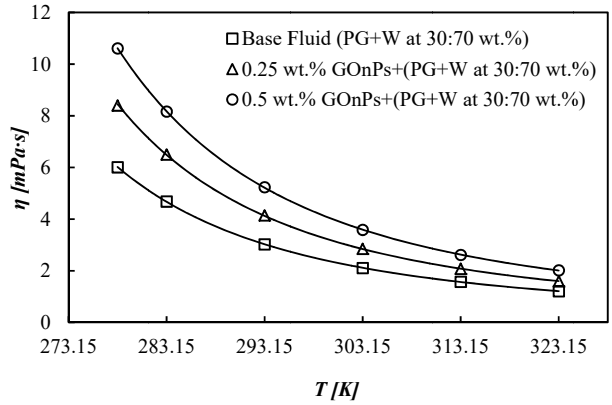

Figure 5 Temperature dependence of dynamic viscosity of GOnPs in (PG+W) at (30:70) wt.%. (—) VFT equation.

As it can be observed, both base fluids exhibit a Newtonian behavior overall the analyzed concentration, temperature and shear rate ranges. Our experimental results for the two base fluids were also compared with previous literature data [22]. Absolute average deviations lower than 1.3% and 3.5% were found for the (propylene glycol + water) mixture at (10:90)% and (30:70)% mass ratios, respectively. This good agreement between literature and our measured data for the used base fluids is also shown in Figure 1.

Similarly, both nanofluid sets a Newtonian behavior at the analyzed low concentrations present. The viscosity of the nanofluids and base fluids is strongly dependent on temperature. The increment of the temperature causes that the nanoparticles are motivated more and create more space for them because the weakening of the inter-particles and inter-molecular adhesion forces. Figures 4 and 5 show these temperature dependences of the dynamic viscosities obtained for the GOnPs nanofluid sets based on (PG+W) mixtures at (10:90)% and (30:70)% mass ratios.

The reported decreases in dynamic viscosity with the temperature reach up to 80% which is in agreement to that reported by Sadeghinezhad et al. [23] for aqueous graphene nanoplatelet nanofluids. One of the most used expressions to correlate the temperature dependence of viscosity is the modification of Andrade's equation known as Vogel-Fulcher-Tamman (VFT):

$$\ln \eta(T) = \ln \eta_0 + \frac{C \cdot T_0}{T - T_0} \quad (1)$$

where η_0, C, and T_0 are the adjustable parameters. The values of these three fitting parameters are gathered for the two studied nanofluid sets in Table 1. VFT equations provides a good description of the temperature dependence, with *AADs%* lower than 1.7%, as it can also be observed in Figures 4 and 5.

Table 1 η_0, *C,* and T_0 coefficients as well as *AADs%* and standards deviations from Vogel-Fulcher-Tammann (VFT) correlation, equation (1), for the two studied nanofluid sets.

	Base Fluid (0 wt.%)	**0.25 wt.%**	**0.5 wt.%**
	GOnPs/(PG+W at 10:90 wt.%)		
η_0 [mPa·s]	0.0948	0.0141	0.0134
C	236.62	777.46	778.19
T_0 [K]	1.145	5.651	5.382
AADs%	0.74	0.36	1.7
s [mPa·s]	0.03	0.01	0.07
	GOnPs/(PG+W at 30:70 wt.%)		
η_0 [mPa·s]	0.0493	0.0618	0.0684
C	431.78	431.95	461.22
T_0 [K]	2.293	2.269	2.470
AADs%	0.20	0.43	0.27
s [mPa·s]	0.008	0.04	0.02

On the other hand, the loading of the graphene oxide nanoplatelets increases the friction and flowing resistance of fluids leading to a viscosity increment. These increases of the dynamic viscosity in relation to base fluids, i.e. $(\eta_{nf}-\eta_{bf})/\eta_{bf}$, as a function of the temperature are shown for the two concentrations of GOnPs in (PG+W) at (10:90)% and (PG+W) at (30:70)% mass ratios in Figure 6 and Figure 7, respectively.

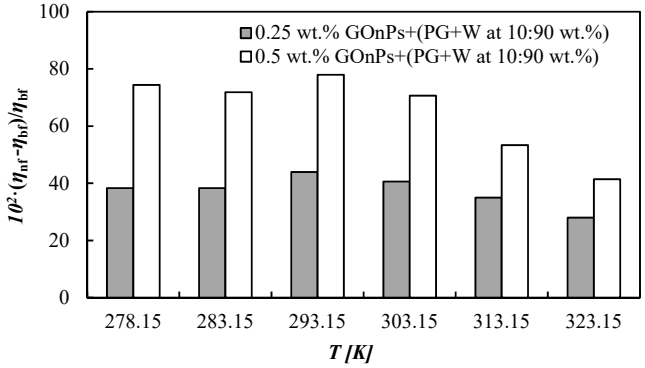

Figure 6 Dynamic viscosity increases of GOnPs in (PG+W) at (10:90)% mass ratio.

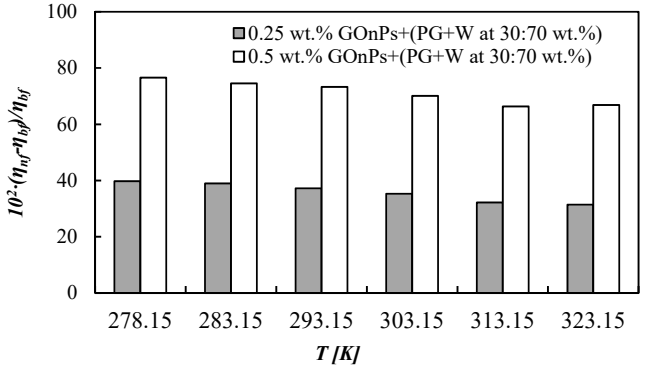

Figure 7 Dynamic viscosity increases of GOnPs in (PG+W) at (30:70)% mass ratio.

As it can be observed, maximum viscosity increases reach up to 44% and 78% at the 0.25% and 0.5% mass concentrations, respectively. Furthermore, the rises in viscosity due to the loading of GOnPs show a downward trend with the increasing temperature. This trend can be due to the fact that the surface charge density rises when the temperature increases. In order to detail the effect of the loading of GOnPs within the analyzed nanoparticle concentration range, in Figure 8 the $\eta(\varphi)$ curves are shown at the different temperatures for the 10:90 wt.% nanofluids, as an example.

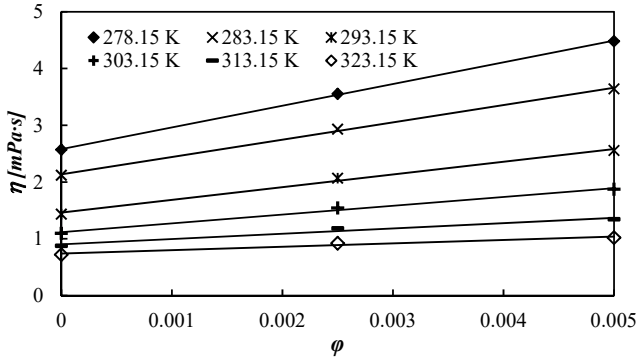

Figure 8 Concentration dependence of the dynamic viscosity of GOnPs/(PG+W at 10:90 wt.%). (—) equation (2).

This concentration dependence is also similar to that exhibited by the studied GOnPs/(PG+W 30:70 wt.%) nanofluids. The slopes of the linear fits of GOnPs/(PG+W 10:90 wt.%) and GOnPs/(PG+W 30:70 wt.%) are gathered in Figure 9.

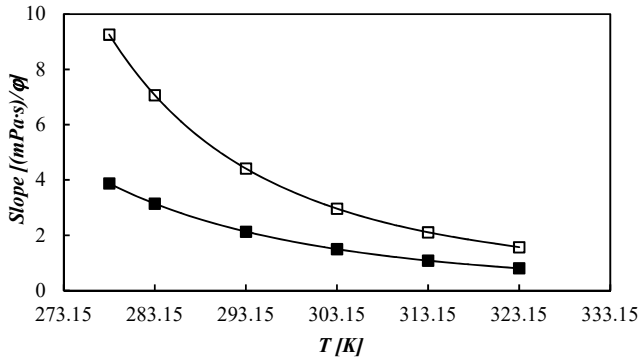

Figure 9 Slope of the linear $\eta(\varphi)$ curves against temperature: (■) GOnPs/(PG+W at 10:90 wt.%) and (□) GOnPs/(PG+W at 30:70 wt.%).

As shown in Figure 9, both slope values present exponential dependences with temperature. The nanofluid set based on (PG+W at 30:70%) exhibits slopes twice as high as those of the GOnPs/(PG+W at 10:90%) nanofluids within the analyzed temperature range.

The temperature and concentration dependences of the two types of studied nanofluids can be described by using the following equation, proposed in this work:

$$\eta = A\, e^{\frac{B}{T}} \cdot \varphi + \eta_0\, e^{\frac{C T_0}{T - T_0}} \qquad (2)$$

where φ is the nanoparticle mass fraction, T is the temperature in K, and A and B are the fitting parameters. η_0, C and T_0 parameters were taken from Table 1. The obtained coefficients by using this expression for each nanofluid set together with the *AADs%* and standard deviations are gathered in Table 2.

Table 2 A and B coefficients as well as *AADs%* from equation (2) for the two studied nanofluids sets.

Parameters	**Nanofluid set**	
	GOnPs/(PG+W 10:90 wt.%)	GOnPs/(PG+W 30:70 wt.%)
A [mPa·s]	0.0040	0.0012
B [K]	3190.83	3764.03
AADs%	2.0	0.92
s [mPa·s]	0.05	0.06

Figure 8 shows the goodness of this equation correlating the $\eta(\varphi, T)$ curves of both nanofluid sets. The new equation allows describing the viscosity behavior of the analyzed glycolated water suspensions of functionalized graphene nanoplatelets with similar deviations to that provided by the well-known Vogel-Fulcher-Tamman equation. Moreover, it is noteworthy that five fitting parameters are necessary for each nanofluid set by the proposed equation while nine are needed when using VFT.

CONCLUSIONS

A DHR-2 rotational rheometer of TA Instruments with concentric cylinder geometry was checked in detail in order to determine the flow behavior in a wide temperature and shear rate range. Good agreements were found between our experimental viscosity values for the Newtonian fluids propylene glycol, Kryptox GLP 102 oil, propylene glycol + water mixture at (10:90)% and propylene glycol + water at (30:70)% in the temperature range from (278.15 to 333.15) K and those previously published in the literature. The rheological behavior of two types of glycolated water suspensions of functionalized graphene nanoplatelets has been explored by using the mentioned device at nanoadditive concentrations up to φ= 0.005 in mass.

The two sets of nanofluids show a Newtonian behavior overall the analyzed concentration and temperature ranges at shear rates up to 100 s^{-1}. For all analyzed nanofluids the diminutions in dynamic viscosity with increasing temperature reach up to 80%. The loading of the graphene oxide nanoplatelets linearly increases the viscosity and these worsening in relation to the base fluid range from (28 to 44)% and from (41 to 78)% for φ= 0.0025 and 0.005, respectively. A relationship between viscosity, nanoadditive concentration and temperature is proposed in this work which allows describing the $\eta(\varphi, T)$ functions with deviations less than 0.07 mPa·s which are similar to those exhibited by $\eta(T)$ curves employing VFT equation.

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