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EFFECT OF SURFACTANTS IN THERMAL CONDUCTIVITY AND VISCOSITY OF WATER- ETHYLENE GLYCOL BASED MWCNT NANOFLUIDS

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Abstract. *This study presents a combined experimental and theoretical analysis of the thermophysical proprieties of Multi Wall Carbon Nanotubes (MWCNT) nanofluids, using as base fluid a mixture of 50:50 water-ethylene glycol in presence of N-Methyl-2-Pyrrolidone (NMP) and Polyvinylpyrrolidone (PVP) surfactants. It were used three different mass concentrations, 0.5%, 1.0% and 1.5% for teach surfactant. All of the samples have the same mass concentration of MWCNT (0.1%). The thermal conductivities of the nanofluids samples were measured using a transient hot bridge method, and for the viscosity was used a Couette type viscometer. Results shown that the thermal conductivities of the nanofluid solutions decreased with increasing surfactant concentrations. Carbon-based nanofluids with PVP had better thermal conductivity. However, PVP presents the highest increments in viscosity.*

Keywords: *Surfactant, Nanofluid, MWCNT, Thermal conductivity, viscosity*

1. INTRODUCTION

The optimization of heat transfer devices is a common practice, which primarily seeks to improve performance, to reduce dimensions, and, consequently, to reduce the heat exchanger cost and, sometimes, weight (Cárdenas, *et al.*, 2015). In this sense, the improving of the thermophysical proprieties of conventional cooling fluids through the addition of particles at nanometric scale (nanofluids) are shown as a promising solution. This concept was introducing by Choi (1995), were the nanofluids are defined as colloidal suspensions of nanometer-sized (≥100 nm) materials (nanoparticles, nanofibers, nanotubes, nanowires, nanorods, and nanosheet) dispersed in conventional fluids (viz., water, ethylene glycol, engine oil, etc.). While the thermal conductivities of nanofluids has shown to be higher than those of their respective base fluids, the stability of the nanofluids has remaining as one of the biggest challenges of this technology, limiting their applications in some cases. Unstable nanofluids may causes pipes clogging and thermal performance deterioration. For this reason, recently the scientist community has increase their efforts researching new methods that allows improving stability and particle dispersion in the nanofluids. However, carbon nanotubes (CNTs) have hydrophobic characteristics and cannot be easily dispersed in most important heat transfer working fluids (such as distilled water (DW) or ethylene glycol) without the use of a surfactant (Kim, *et al.*, 2018).

Many kinds of surfactants are used with nanoparticle suspensions to increase the dispersion and stability of nanofluids. For example, Sánchez-Coronilla, *et al.*, 2018 found that the uses of benzalkonium chloride (BAC) as surfactant enhance the stability of a nanofluid composed by NiO particles on a base fluid of diphenyl oxide mixture with biphenyl. Yang, *et al.*, 2011 also studied the stability of Al_2O_3 nanoparticles with sodium dodecyl benzene sulfonate (SDBS) in the ammonia-water solution. Das, *et al.*, 2018 uses four different surfactant cetyl trimethyl ammonium bromide (CTAB), acetic acid (AA), (SDBS), and sodium dodecyl sulfate (SDS) to systemizes TiO_2 water-based nanofluids. They found an enhancement in thermal conductivity of 5.8% over that of the base fluid, for the SDS-surfacted nanofluid at 1% volume fraction. Choi, *et al.*, 2018, observed that the SDBS is the most appropriate surfactant used to create water-based MWCNT nanofluids in function of the suspension stability and high absorption of the sunlight characteristics. Also, Gangadevi, *et al.*, 2018 obtained an increase of the thermal conductivity of CuO/water and Al2O3/water nanofluids using SDBS surfactant. However, another works (Xuan, *et al.*, 2013 and Kim, *et al.*, 2018) that also uses SDBS reveals that the surfactant remarkably affects transport properties and suppresses the heat transfer enhancement effect of the nanofluids. The effects of the Polyvinylpyrrolidone (PVP) was also investigated in different works. Leong, *et al.*, 2018 presents an improvement of 9.8% in the thermal conductivity of an ethylene glycol/water-based hybrid nanofluid containing of Cu-TiO2 and PVP. Xia, *et al.*, 2014 and T.S., *et al.*, 2018 demonstrate that Al_2O_3 nanofluid using PVP shown better results in the enhancing of thermal conductivity when compared to other surfactants. Koca, *et al.*, 2017 found that the thermal conductivity of Ag-water nanofluids decreases with the increasing of Ag and PVP concentrations. Cárdenas, *et al.*, 2017, Sadeghinezhad, *et al.*, 2016 and Sun, *et al.*, 2013 among others, studied the performance of different carbon nanofluids using N-Methyl-2-Pyrrolidone (NMP) as surfactant.

Although the surfactants are used to improve the dispersibility of the nanoparticles in the base fluid, avoiding the re-agglomeration of the particles, there are reports that their presence in the nanofluids interferes with thermal conductivity and viscosity (Oliveira et al. 2017).

In this work, are studied the effects on the stability and thermophysycal proprieties of the N-Methyl-2-Pyrrolidone (NMP) and the Polyvinylpyrrolidone (PVP) as surfactants in a dispersion of Multi Wall Carbon Nano-Tubes (MWCNT) in a base fluid of a 50-50 mixture of water with ethylene glycol.

2. METHODOLOGY

Before synthesizing the samples to be evaluated and in order of determine the influence of the surfactant on the stability of the mixture and on the thermophysical properties of the nanofluids, it was determined that 13 fluid samples would be produced. Firstly, seven base fluid samples using a mixture of ethylene glycol and water with a weight concentration of 50% of water and 50% of ethylene glycol and three different concentrations of N-methyl-2-pyrrolidone (NMP) and polyvinylpyrrolidone (PVP) as indicated in Tab. 1. The other six samples will be producing adding carbon nanotube MWCNT to the base fluids with a mass concentration of nanoparticles of 0.1%.

Table 1. Description of the produced fluids.

Fluids	Surfactant	Surfactant ϕ_{WT} (1) [%]	Nomenclature
H_2O+EG	-	-	REF
	NMP	0,5	NMP1
		1,0	NMP2
		1,5	NMP3
	PVP	0,5	PVP1
		1,0	PVP2
		1,5	PVP3
MWCNT/(H_2O+EG)	NMP	0,5	MW_NMP1
		1,0	MW_NMP2
		1,5	MW_NMP3
	PVP	0,5	MW_PVP1
		1,0	MW_PVP2
		1,5	MW_PVP3

(1) ϕ_{WT} (Mass Concentration)

Nanomaterials were purchased from Nanostructures & Amorphous Material Inc., and manufacturer declared their physical properties as presented in Tab. 2.

Table 2. Basic properties MWCNT.

Morphology	Tubes
Average particle size	External diameter 20-40 nm Internal diameter: 5-10 nm Length: 5-15 µm
Powder purity	> 95%
Specific surface area	40-600 [m²/g]
Specific mass	2100 [kg/m³]
Specific heat	0,710 [kJ/kgK]
Thermal Conductivity	50-200 [W/m.K]

2.1 Production of sample fluids

The production method used in the present work, is mostly know as Two-Step Method. In this method, the nanoparticles are initially synthesized as ultrafine dry powder and are then dispersed in the base fluids using extra external energy, which can be supplied with the aid of intensive magnetic stirring, ultrasonic agitation, high shear rate mixing, or homogenization by high pressure. Therefore, the nanofluids produced in this work were the result of a process of dispersion, sonication and homogenization of nanoparticles in powder form within the base fluids. Thus, to produce the nanofluid samples, a routine described by Fig. 1, which is also being applied in the synthesis of all samples.

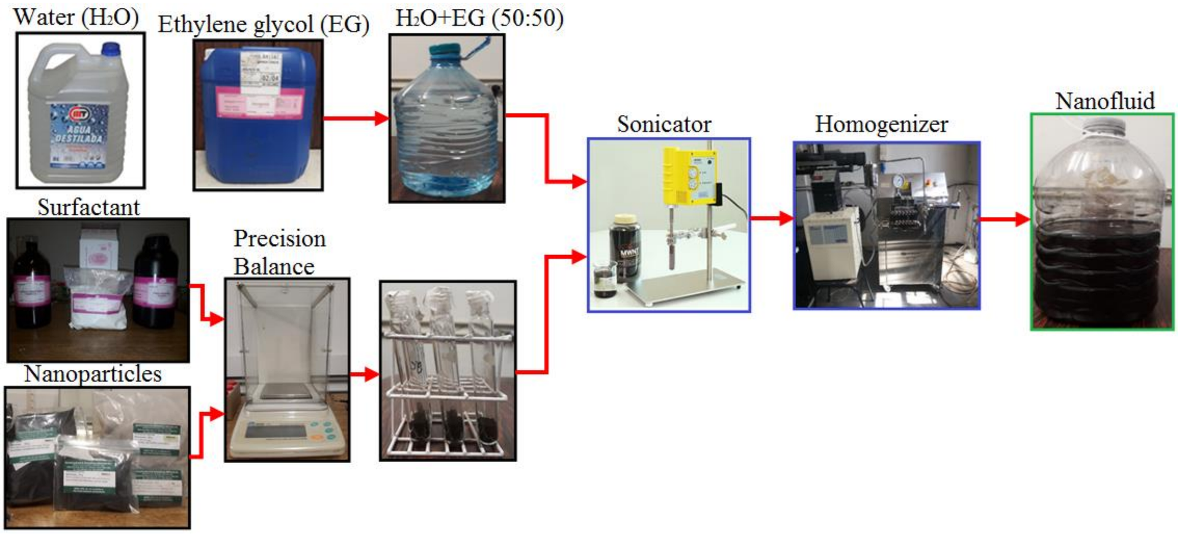


Figure 1. Nanofluids production process

The process begins with the mixture of ethylene glycol and water with a concentration of 50% by mass of water and 50% of ethylene glycol. The required masses of base fluid (H2O + EG), surfactant and nanoparticles were measured with a precision balance. Then, the base fluid was mixed with the surfactant by stirring. The nanoparticles were added to the mixture (base-surfactant fluid) and sonicated applying a power of 750 W with a frequency of 20 kHz. This sonication process was performed for 30 to 35 minutes, controlling for temperature rise (<50 ° C). In this way, a possible degradation of the surfactant which may impair the stability of the dispersion is prevented. Once the sonication process is finished, the samples were submitted to a homogenization process, under 400 bar of pression. The stipulated time for the homogenization process varies between 40 and 50 minutes per sample.

2.2 Viscosity measurements

The specific mass and the dynamic viscosity of the nanofluid and base fluid samples were measurement with the Anton Paar viscometer (Stabinger ™ Model SVM ™ 3000), shown in Fig. 2. The operating principle of the equipment is a modification of the Couette system.

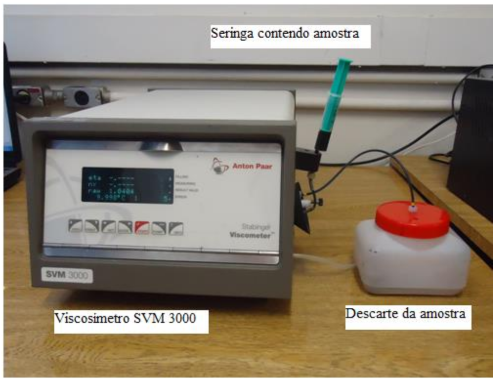


Figure 2. Experimental equipment to measure the specific mass and the dynamic viscosity.

2.3 Thermal conductivity Measurements

The thermal conductivity was measured with a thermal properties analyzer produced by Linseis THB1 - Transient Hot Bridge (Fig. 3). The THB method or hot bridge transient method is used to measure the thermal properties of the materials. This method is an evolution of the transient hot wire method (THW) which follows the guideline of the standard (DIN EN 993-14, DIN EN 993-15).

Figure 3. Experimental equipment to measure the thermal conductivity.

3. RESULTS AND DISCUSION

3.1 Validation of the measurements

All the measurement were performed in a temperature range from 10 °C to 50 °C, using increments of 10 ° C. The experimental results of viscosity and thermal conductivity obtained for the reference base fluid sample (REF) were compared to the theoretical data from the Engineering Equation Solver (EES) software. According to Fig. 4, the experimental results presents a good agreement with the theoretical values, showing a maximum deviation of 2.8% for the viscosity and 1.64% for the thermal conductivity.

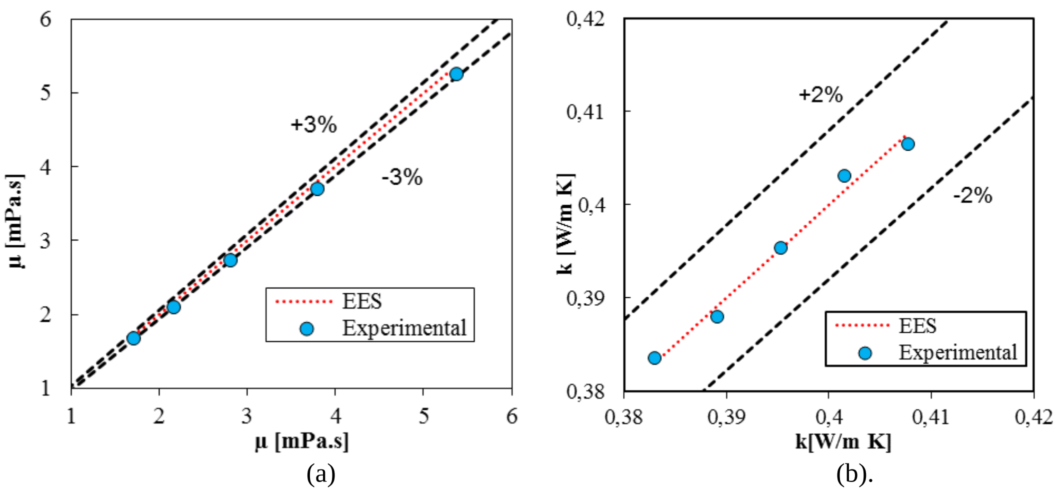


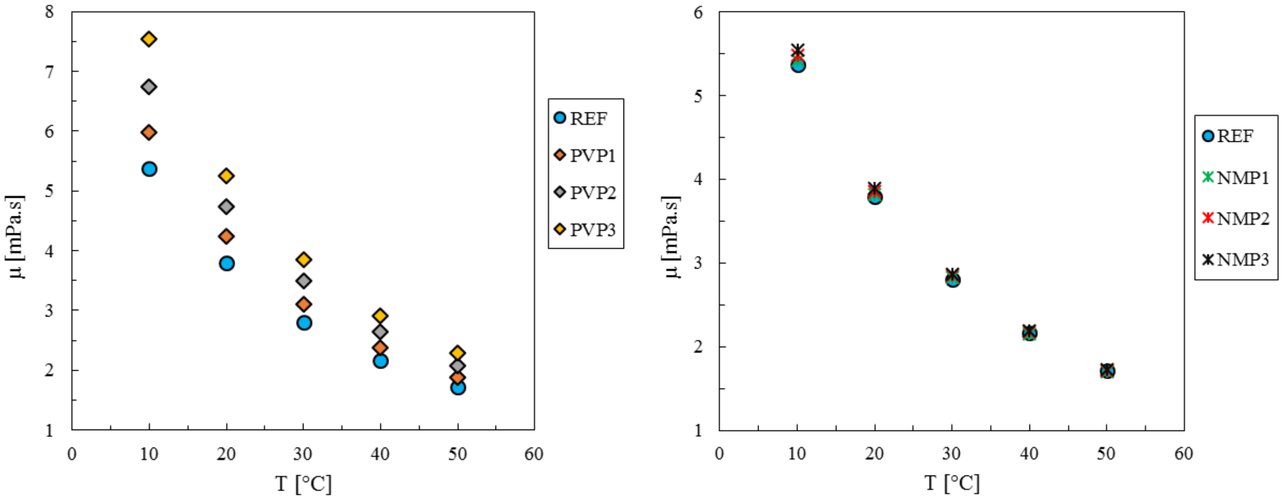
Figure 4. Validation of the experimental results for the reference base fluid a). Dynamic viscosity. b). Thermal conductivity.

3.2 Viscosity Results

The results of the viscosity measurement as a function of temperature for the samples produced only with the surfactant addition (PVP and NMP) are shown in Fig. 5 (a) and (b). It can be seen from Fig. 5 (a) that the PVP1 sample, PVP2 sample and the PVP3 presented an average increase in the viscosity of 11%, 24% and of 37%, respectively. Therefore, an increase in viscosity proportional to the addition of surfactant may be observed.

In Fig. 5 (b) it can be seen that all samples produced only with addition of N-methyl-2-pyrrolidone (NMP) had slight viscosity increments. That average of the increments was 0.3% for NMP1 samples, 1.3% NMP2 samples and 2% for the NMP3 sample. Thus, it was observed that the addition of polyvinylpyrrolidone (PVP) results in higher increases in viscosity of the base fluids when compared to the increments observed with the addition of N-methyl-2-pyrrolidone (NMP).

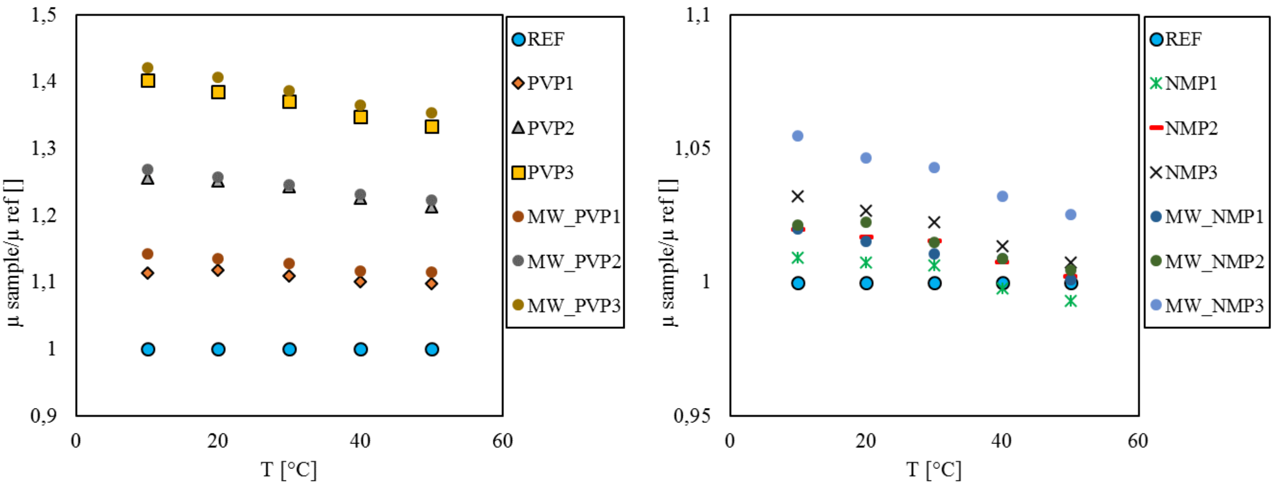
Figures 6 (a) and (b) show the effective viscosity as a function of temperature of the samples with only surfactant and with the nanoparticles. The effective viscosity shown in Fig. 6 (a) and (b) uses as base of comparison the viscosity of the reference base fluid (H2O:EG).



(a) (b)

Figure 5. Experimental viscosity of base fluids and base fluid with surfactant. (a) Polyvinylpyrrolidone (PVP). (b) N-methyl-2-pyrrolidone (NMP).

Therefore, Fig. 6 (a) shows the results of the effective viscosity of samples containing polyvinylpyrrolidone (PVP). Nanofluid samples of carbon nanotubes with the same mass concentration of nanoparticles (0.1%) and different surfactant mass concentrations MW_PVP1, MW_PVP2 and MW_PVP3 shown average increments of 13, 25 and 35% respectively. Figure 6 (b) shows the results of the effective viscosity of N-methyl-2-pyrrolidone (NMP) samples. It can be observed average increments of 1%, 1.5% and 4% for MW_NMP1, MW_NMP2 and MW_NMP3 respectively. Because the addition of surfactant (NMP) did not have a significant contribution in increasing the viscosity of the samples, the contribution in increasing the viscosity caused by the addition of the nanoparticles can be observed.



(a) (b)

Figure 6. Effective viscosity of the samples. (a) with Polyvinylpyrrolidone (PVP). (b) with N-methyl-2-pyrrolidone (NMP).

3.3 Thermal Conductivity Results

The results of the thermal conductivity measurement as a function of temperature for the samples produced only with the surfactant addition (k_PVPn and k_NMPn) are shown in Fig. 7 (a) and (b). It can be seen from Fig. 7 (a) that the sample PVP1 with concentration of (PVP) of 0.5% presented a decrease in the thermal conductivity in average of 0.9%. The sample PVP2 with a mass concentration of 1% of (PVP) had a decrease in the conductivity of 1.4%, and the PVP3 sample with a mass concentration of 1.5% of (PVP) showed an increase in viscosity on average of 1, 9%.

On the other hand, as indicated in Fig. 7 (b) all samples produced only with N-methyl-2-pyrrolidone (NMP) presented higher thermal conductivity decreases. For NMP1 samples, the average decrease in conductivity was 4%, for the sample NMP2, the decrease in conductivity was 4.7%, and for the sample NMP3 the decrease in the thermal conductivity was on average 5.1%.

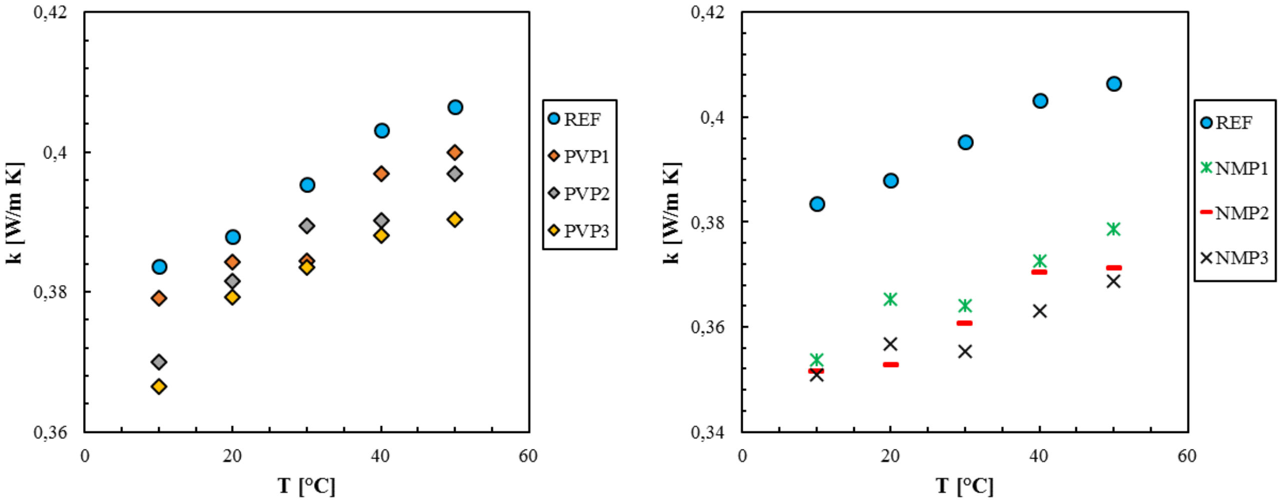


Figure 7. Experimental thermal conductivity of base fluids and base fluid with surfactant. (a) Polyvinylpyrrolidone (PVP). (b) N-methyl-2-pyrrolidone (NMP).

Therefore, it can be observed that the thermal conductivity of the base fluid decreases proportionally with the addition of surfactant. Also, it is observed that the addition of N-methyl-2-pyrrolidone (NMP) results in higher decreases in the thermal conductivity of the base fluid when compared to decreases observed with the addition of polyvinylpyrrolidone (PVP).

Figure 8 presents the effective conductivity as a function of temperature for the carbon nanotube nanofluid samples having surfactant (MW_PVPn and MW_NMPn). Thus, the effective conductivity shown in Fig. 8 uses as base of comparison the thermal conductivity obtained for the reference base fluid (k_H2O: EG).

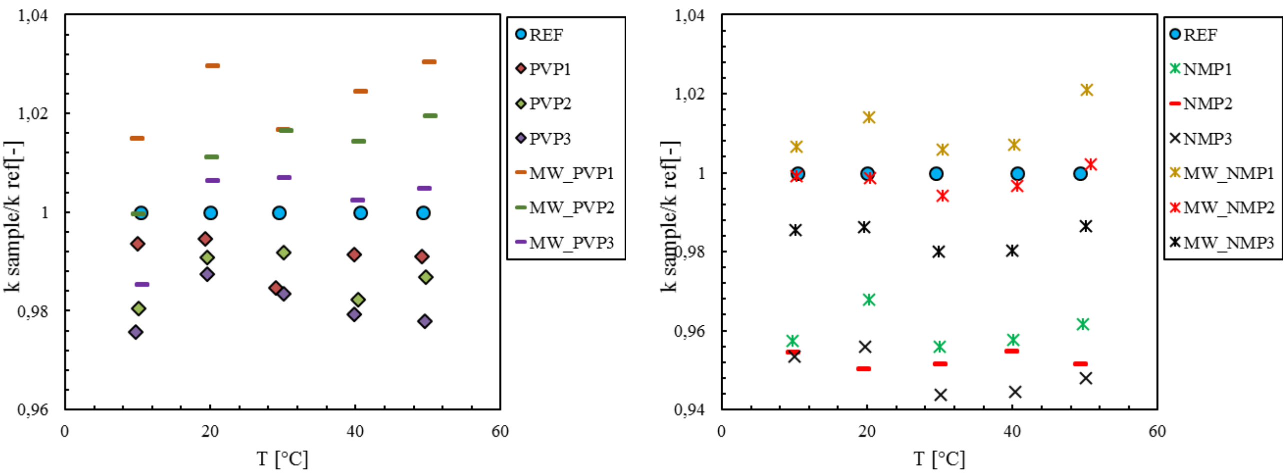


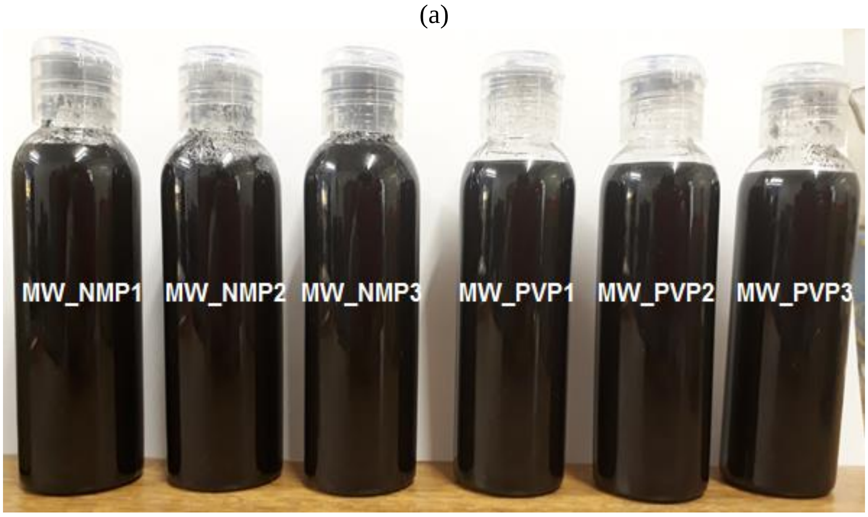
Figure 8. Effective thermal conductivity of the samples. (a) with Polyvinylpyrrolidone (PVP). (b) with N-methyl-2-pyrrolidone (NMP).

Therefore, it can be observed that samples of carbon nanotube nanofluids (MW_PVP1, MW_PVP2 and MW_PVP3) with the same mass concentration of nanoparticles (0.1%), which have different concentrations of surfactant polyvinylpyrrolidone (PVP) of 2.3%, 1.2% and 0.2% respectively. The sample of nanofluids of carbon nanotube (MW_NMP1) that used as surfactant N-methyl-2-pyrrolidone (NMP) had an increase in the thermal conductivity in average of 1.1%. However, the samples (MW_NMP2 and MW_NM3) showed decreases averaging 0.2% and 1.6% respectively, indicating that the addition of the nanoparticle did not compensate for the negative effect of surfactant addition.

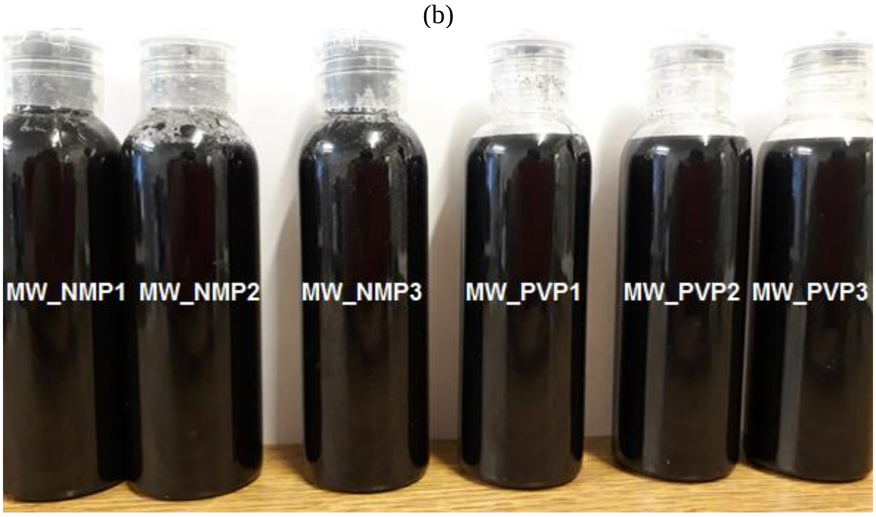
3.4 Stability

In the evaluation of nanofluid stability, there is no standardized technique or criterion. However, in the literature the commonly used methods are: Zeta potential analysis and spectral absorption analysis. It is important to note that, in this work, such methods are not used to verify stability. However, changes in the stability of the samples after production was photographed in a time sequence. Thus, Figs. 9 (a), (b) and (c) show the carbon nanofluids samples one hour, 10 days and 30 days after production, respectively.

(a)



(b)



(c)

Figure 9. Images of nanofluids registered a) After one hour. b) After 10 days. c) After 30 days, of the production

In these images, it can be seen that all samples are visually stable. 10 days after sample production, all carbon nanofluids (MWCNT / (H2O + EG)) were still visually stable, as can be seen in Fig 9 (b). However, after 30 days of production shown in Fig. 9 (c), they began to suffer a slight sedimentation. In the samples with N-methyl-2-pyrrolidone as surfactant, was observed some particles agglomeration.

4. CONCLUSIONS

In this work, two types of surfactant (N-Methyl-2-Pyrrolidone (NMP) and the Polyvinylpyrrolidone (PVP)) were used to evaluate the effect of this on the stability of Multi Wall Carbon Nano-Tubes (MWCNT) nanofluids and their thermophysical properties.

Samples PVP1, PVP2 and PVP3 showed viscosity increases on average of 11%, 24% and 37% respectivelly. Therefore, an increase in viscosity proportional to the addition of surfactant may be observed. However, samples NMP1, NMP2 and NMP3 showed slight viscosity increments, less than 2%. Thus, it was observed that the addition of polyvinylpyrrolidone (PVP) results in higher increases in the viscosity of the base fluids when compared to the increments observed with the addition of N-methyl-2-pyrrolidone (NMP) using the same mass concentrations of surfactant.

It can be observed that the samples PVP1, PVP2 and PVP3 presented a decrease in the thermal conductivity in average of 0.9%, 1.4% and 1,9% respectively. On the other hand, all samples produced only with N-methyl-2-pyrrolidone (NMP) showed higher thermal conductivity decreases, ie 4% for the NMP1 sample, 4.7% for the NMP2 sample and of 5.1% for sample NMP3. Therefore, it can be observed that the thermal conductivity of the base fluid decreases proportionally with the addition of surfactant. In addition, it is observed that the addition of N-methyl-2-pyrrolidone (NMP) results in higher decreases in the thermal conductivity of the base fluid when compared to decreases observed with the addition of polyvinylpyrrolidone (PVP).

One month after the production of all samples of nanofluids presented a slightly sedimentation of nanoparticles. However, samples using N-methyl-2-pyrrolidone (NMP) as surfactant presented agglomeration among the particles.

5. ACKNOWLEDGEMENTS

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