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**Experimental study on thermophysical properties of alumina Nanoparticle Enhanced
Ionic Liquids**

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Abstract:

In this experimental study, several alumina Nanoparticle Enhanced Ionic Liquids were prepared and studied in regard to their stability, pH, density and thermal conductivity. These new fluids were manufactured by dispersing aluminium oxide nanoparticles in different mixtures based on water and 1-ethyl-3-methylimidazolium methanesulfonate ionic liquid. Furthermore, thermophysical properties (density, thermal conductivity) of pure and binary mixtures with water and 1-ethyl-3-methylimidazolium methanesulfonate were studied in order to select and propose base fluids to design new advanced heat transfer fluids. The pH of the dispersions was determined as around 8.0 - 8.5. In regard to density, the overall [C₂mim][CH₃SO₃] density is higher by 25% than that of water and the influence of ionic liquid density over the mixtures was found to be much higher than that of water, while for the alumina Nanoparticle Enhanced Ionic Liquids the density respects classical equations. Evaluation of thermal conductivity revealed an increase of up to 13% in thermal conductivity when nanoparticles are added to the base fluids and new correlations based on mass fraction and temperature were proposed.

Keywords: Nanoparticle Enhanced Ionic Liquids (NEILs); thermal conductivity; density; pH; ionic liquids; Al₂O₃ Nanoparticles

Highlights

- ionic liquid-water mixtures were prepared
- pH of developed new fluids is measured and good stability is noticed
- Al_2O_3 NEILs density is experimentally examined and good agreement with existing equations was noticed
- Al_2O_3 NEILs thermal conductivity is experimentally examined and an enhancement was noted
- Al_2O_3 NEILs thermal conductivity correlations are proposed

Nomenclature

k	thermal conductivity, W/m K
T	temperature, K
R^2	accuracy of the fitted equations, -
x	mole fraction, -

Greek symbols

ρ	density, g/cm ³
ϕ	particle fraction, -

Abbreviations

BET	Brunauer–Emmett–Teller theory
HTF	heat transfer fluid
IL	ionic liquid
NEIL	nanoparticle enhanced ionic liquid
W	water

Subscripts:

bf	refers to base fluid
inf	refers to NEIL
m	refers to mass concentration
p	refers to particle
r	relative
vol	refers to volume
wt	refers to weight

1. Introduction

Since industrial revolution, fluids have been used in great part of energy transformation processes to carry and transfer thermal energy. Currently concern about the use of renewable and non-pollutant energy sources have encouraged worldwide researchers to design new eco-friendly heat transfer fluids, HTFs, fulfilling international commitments such as COP21 in December 2015 (*Note: The Paris Agreement, also known as COP21, is an agreement among the leaders of more than 170 countries to reduce greenhouse gas emissions and limit the global temperature increase to below 2 °C above pre-industrial levels by the year 2100.*). Most common HTFs used in the literature include water, glycols, mineral and synthetic oils, ionic liquids or molten salts [1].

Over the last century, ionic liquids, ILs, have been employed as solvents for synthesis and catalysis due to their tunable physicochemical properties [2-4]. In addition, ILs present very low vapor pressure, high thermal stability, and non-volatility [3]. These characteristics, especially their low vapor pressure and non-volatility, make them good candidates as HTFs in renewable energy systems [5]. Also, several investigations aimed at the evaluation of the toxicity of ILs have been performed, reporting very high lethal doses and no-noticeable chronic effects [6]. Combined effects of non-toxicity and non-volatility ensure safety use of ILs in industrial plants and thermal energy systems, with no effect over people nor the environment. High cost of ILs manufacturing, motivated by the absence of large-scale production, is the most considerable handicap to extend their general use as HTFs [6].

Essentially, ILs are molten salts at room temperature (below 373 K), therefore, their structure is comprised by positive and negative ions (named as cation and anion, respectively). Some ILs are water-miscible [7], allowing the possibility of have two different structures, “IL-type” and “water-type” depending on the fraction of water present in the mixture [8]. Concerning

the solubility of ILs with water, the selection of the anion is the most determining factor; even so, hydrophobic ILs are in fact also hygroscopic [9, 10].

Blending good thermophysical properties of ILs and recent advancements in the field of nanofluids it is possible to develop new improved HTFs: the so-called nanoparticle enhanced ionic liquids, NEILs [5]. The chemical structure of ILs contribute to the stability of dispersed nanoparticles due to the creation of an electrostatic layer surrounding them [11]. Nieto de Castro et al. [12, 13] designed several NEILs based on imidazolium-type pyrrolidinium-type ILs, using multiwalled carbon nanotubes, MWCNTs, and obtained thermal conductivity enhancements up to 26% when 3% w/w of MWCNTs is dispersed in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. Enhancement of 10% in thermal conductivity were found by Wang et al. [14] in NEILs containing 0.03% w/w graphene. Xie et al. [15] studied thermal conductivity, viscosity and density of NEILs based on 1-ethyl-3-methylimidazolium diethylphosphate and its mixtures with water by dispersing MWCNTs, obtaining up to 9.7% of enhancement in thermal conductivity compared with the base ILs. Paul et al. [5] had dispersed Al_2O_3 nanoparticles in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at volume fractions of 0.18%, 0.36% and 0.9%. They reported density, viscosity, thermal conductivity and heat capacity measurements and determined heat transfer coefficients by using an experimental test bench. An enhancement of 11% in thermal conductivity was found in case of 0.9% v/v of nanoparticles. Heat transfer behavior of several NEILs containing MWCNTs were studied by França et al. [16].

Hasse et al. [17] showed the influence of 3 different cations in 1-ethyl-3-methylimidazolium-based ILs by determining their viscosity, interfacial tension, density, and refractive index. Concerning density behavior, they found out that the chemical structure of the anions are more relevant than their molecular weight depending on the formation of molecular assemblies [17]. Thermophysical profile of another eight ILs based on the same cation were

reported in 2011 by Freire et al., obtaining density, isobaric thermal expansivity, heat capacity, viscosity, and refractive index [18]. Density and viscosity of this IL have been widely studied in the literature [17-24]. Safarov et al. [22, 23] matched their experimental results with Tait and Vogel-Tamman-Fulcher model, respectively, suggesting new density and viscosity correlations. Stark et al. [25] studied the structure of the mixtures of 1-ethyl-3-methylimidazolium methanesulfonate and water. They concluded that the nonpolar domain of the IL is strongly enough to maintain a IL-type chemical structure up to 0.9 water mole fractions [25].

In this work, thermophysical properties (density, and thermal conductivity) of pure and binary mixtures with water of 1-ethyl-3-methylimidazolium methanesulfonate were studied in order to select and propose base fluids to design NEILs as new advanced HTFs. These NEILs were manufactured by dispersing aluminium oxide nanoparticles in the selected base ILs at different mass fractions. Up to our knowledge, no experimental studies were carried out for NEILs based in the selected base fluids of this work, i.e. 1-ethyl-3-methylimidazolium methanesulfonate, $[C_2mim][CH_3SO_3]$, and $[C_2mim][CH_3SO_3]$ + water binary mixture.

2. Experimental

2.1. Materials

For this experimental study, 1-ethyl-3-methylimidazolium methanesulfonate $[C_2mim][CH_3SO_3]$ (CAS 145022-45-3) ionic liquid with $\geq 95\%$ purity and water content less than 0.5% w/w and Al_2O_3 nanoparticles with a declared average size of 50 nm were acquired from Sigma-Aldrich (St. Louis, USA). The alumina nanoparticles (CAS 1344-28-1) properties, as per manufacturer information are: BET (Brunauer–Emmett–Teller) specific surface area is larger than 40 m²/g, vapour pressure of 1 hPa at 2158 °C, relative density is of

4.00 g/cm³ and molecular weight of 101.96 g/mol. The IL is soluble in water and its main properties given by the manufacturer are in Table 1.

Table 1. Main properties of [C₂mim][CH₃SO₃] IL, as per given by the manufacturer.

CAS Number	145022-45-3
Molecular formula	C ₇ H ₁₄ N ₂ O ₃ S
Molecular weight	206.26 g/mol
Water content	0.029 wt%
Melting point	35°C
Impurities	≤0.5%

Although the melting point of the ionic liquid is declared as 35°C by the manufacturer, its actual state at room temperature is liquid. The same situation was noticed also by Bioucas et al. [24], who worked with 50 kg of [C₂mim][CH₃SO₃] from BASF (under the trade name of Basionics® ST35). Their ionic liquid was originally in solid state and they melted it at 303.15 K remaining in a liquid state for about 2 years.

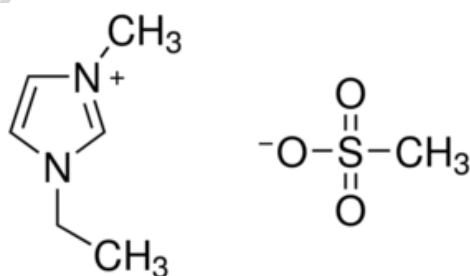


Figure 1. Chemical structure of 1-ethyl-3-methylimidazolium methanesulfonate

Table 2 contains an outline of the prepared new fluids while this experimental study consists in two parts: first focus on the selection of the base fluid, thus IL and binary IL + W mixtures

at different water mole fraction were prepared; and on the other part, the design of dispersions of Al_2O_3 in selected base fluids. More exactly, several binary $[\text{C}_2\text{mim}][\text{CH}_3\text{SO}_3]^+$ water mixtures at different water mole fraction, x_w , were considered to evaluate the water influence in the behavior of proposed mixtures. For the experimental work, it was decided to prepare new fluids, as one can notice in Table 2. Binary mixtures were firstly prepared by adding water to the base IL in the established proportions and secondly, alumina nanoparticles were dispersed in the selected base mixture (see Table 2). So, the binary mixtures are named as $x_w\text{W} + (1-x_w)\text{IL}$, x_w being the mole fraction, with $x_w = 0; 0.25; 0.50; 0.75$ and 1 , while the dispersions are named as $\phi_{\text{wt}}\text{Al}_2\text{O}_3/ (x_w\text{W} + (1-x_w)\text{IL})$, pure IL and $0.25\text{W}+0.75\text{IL}$ being the base fluid. Therefore, the different Al_2O_3 nanoparticle mass concentrations, %wt, of $0.5; 1; 2.5; 5; 10$ and 15 were elaborated. Although several dispersions using IL and the three studied binary mixtures as base fluids were elaborated, we have selected only IL and $0.25\text{W}+0.75\text{IL}$ as base fluids for this research since high instability was noticed for the other two. So, stability of $(0.50\text{W}+0.50\text{IL})$ - and $(0.75\text{W}+0.25\text{IL})$ -based NEILs was not considered acceptable and surfactant addition could be needed.

Table 2. Studied fluids

Fluid type	Code	Mole fraction of water, x_w , -	Mass concentration of alumina, ϕ_{wt} , %
ionic liquid	IL	0.00	0.00
mixtures	0.25W+0.75IL	0.25	0.00
ionic liquid +	0.50W+0.50IL	0.50	0.00
water	0.75W+ 0.25IL	0.75	0.00
NEIL:	0.5% wt $\text{Al}_2\text{O}_3/\text{IL}$	0.00	0.50

dispersion of alumina into pure ionic liquid	1% wt $\text{Al}_2\text{O}_3/\text{IL}$	0.00	1.00
	2.5% wt $\text{Al}_2\text{O}_3/\text{IL}$	0.00	2.50
	5% wt $\text{Al}_2\text{O}_3/\text{IL}$	0.00	5.00
	10% wt $\text{Al}_2\text{O}_3/\text{IL}$	0.00	10.0
	15% wt $\text{Al}_2\text{O}_3/\text{IL}$	0.00	15.0
NEIL: dispersions of alumina into IL - W mixtures	0.5% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$	0.25	0.50
	1% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$	0.25	1.00
	2.5% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$	0.25	2.50
	5% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$	0.25	5.00
	10% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$	0.25	10.00
	15% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$	0.25	15.00

2.2. Preparation

For preparing the binary mixtures between water and ionic liquids (see Table 2), the calculated amounts of the two samples, based on mole fraction, were weighted by using a Sartorius CPA225 (Gottingen, Germany), with accuracy of 1×10^{-5} g, and mixed in a VELP Scientifica ZX3 Advanced Vortex Mixer (Usmate, Italy) for 2 minutes at a power of 15W. NEILs were prepared by dispersing calculated amounts of nanoparticles to obtain the Al_2O_3 mass fraction declared in Table 2. Dispersing the alumina into the base fluid was accomplished with the assistance of an ultrasonic procedure to improve the nanofluid stability and to avoid sedimentation [26]. Nanoparticles further dispersed into the base fluid by using ultrasonic homogenizer Bandelin Sonopuls HD 2200 (Berlin, Germany) at a 200W power during 60 min.

2.3. Characterization and stability

The analysis of morphology and sizes of Al_2O_3 nanoparticles was performed on a transmission electron microscope (TEM) JEOL JEM-1010 (Tokyo, Japan), operating at an acceleration voltage of 100 kV [26]. A drop of as received nanoparticles dispersed in 1-buthanol was deposited on the top of a copper grid covered with Formvar and a carbon layer. Figure 2 shows that the samples appear as quasi-spherical and polydispersed particles.

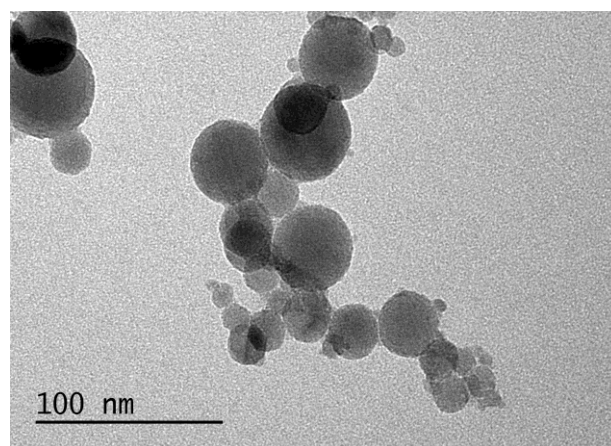


Figure 2. TEM of alumina nanoparticles

The nominal particle sized reported by the manufacturer (~ 50 nm) reflect the average value, however actual particle sizes vary significantly as it is shown in Figure 2 by using TEM where polydispersity size is observed (sizes between 10 and 50 nm). On the other hand, a more realistic situation is indicated through DLS measurements in which average values in dispersion are around 70 nm.

The evaluation of the stability of designed NEILs was performed by means of a Zetasizer Nano ZS (Malvern, UK) using the dynamic light scattering (DLS) technique with a scattering angle of 173° . Following the procedure reported by Cabaleiro et al. [27], in four different cuvettes two samples of 1% wt $\text{Al}_2\text{O}_3/\text{IL}$ and two samples of 1% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$ were deposited, remaining one of each fluid in static conditions and shaking the others every

day prior to the measurement. During more than 20 days, size distribution measurements were performed almost every day, obtaining unimodal size distributions in both NEILs that evolve to bimodal size distributions, as shown in Figure 3. For the IL-based nanofluid, the main peak moves 80 nm to the left in the shaken sample and 200 nm to the left in the static one while appears a peak at 30 nm in both samples. For the 0.25W+0.75IL based nanofluid, the main peak moves 60 nm to the right in the shaken sample and 60 nm to the left in the static one while appears a peak at 100 nm in the shaken sample and at 30 nm in the static one.

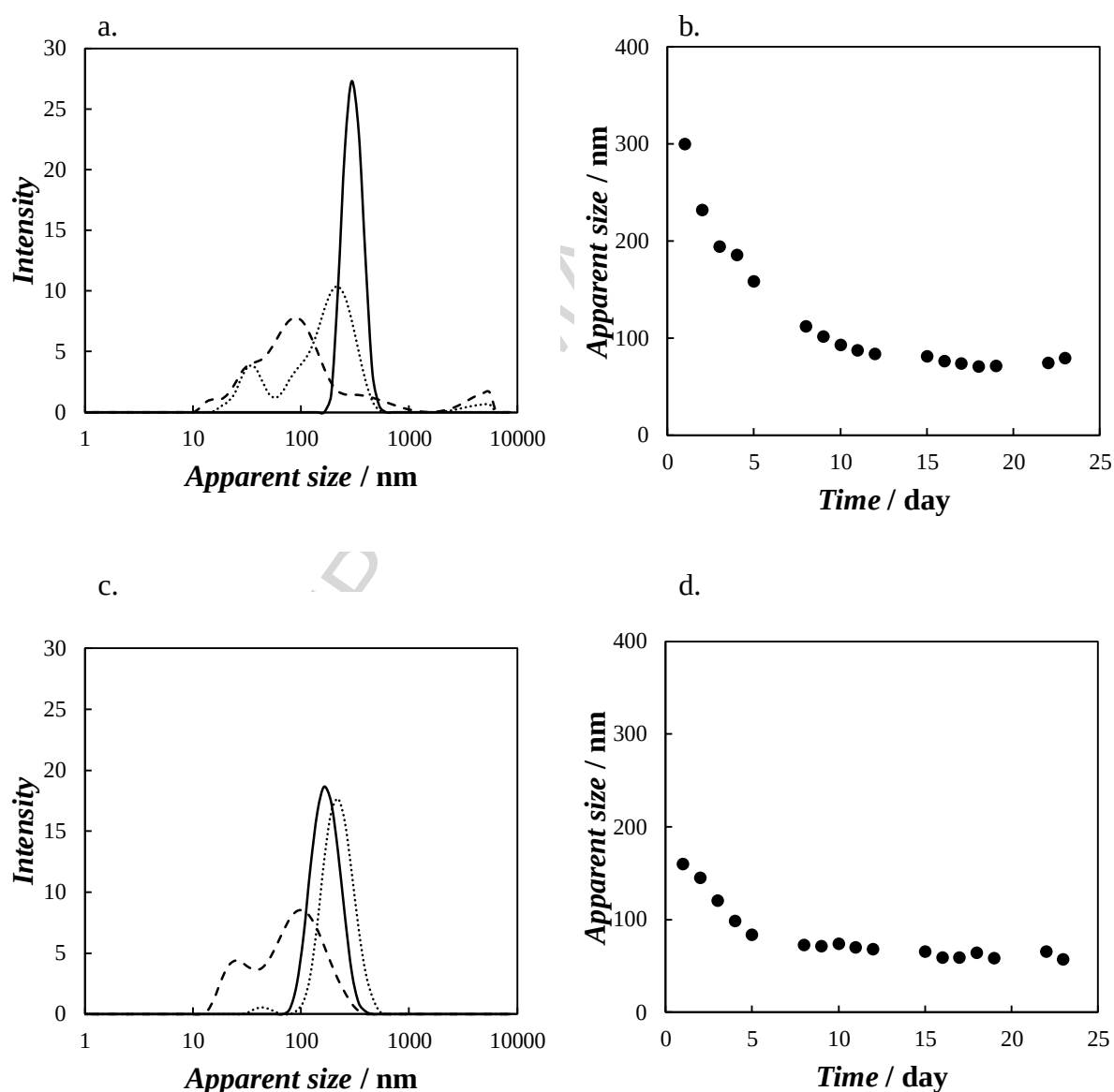


Figure 3. (a) Apparent size distribution of 1% wt $\text{Al}_2\text{O}_3/\text{IL}$: (—) 1st day, (- -) 30th day static sample, and ($\cdots$) 20th day shaken sample. (b) Temporal evolution of apparent size of 1% wt $\text{Al}_2\text{O}_3/\text{IL}$. (c) Apparent size distribution of 1% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$: (—) 1st day, (- -) 30th day static sample, and ($\cdots$) 20th day shaken sample. (d) Temporal evolution of apparent size of 1% wt $\text{Al}_2\text{O}_3/(0.25\text{W}+0.75\text{IL})$.

2.4. Procedures and techniques

The experimental results on new fluids properties involved the determination of the pH, density and thermal conductivity [13, 26, 28-30]. The density was measured between 283.15 K and 313.15 K with a density meter type DMA 500 from Anton Paar (Graz, Austria). Before samples density measurements, a densimeter checking process with a reference fluid was carried out following the procedures described in Żyła et al. [30] and the measurements accuracy was found to be lower than 0.1%. The pH of the samples was determined at ambient temperature with a HACH pH-METRO SENSION + ph3 (Loveland, USA) and the accuracy of measurements was estimated to be within 1%. The fluids thermal conductivity was measured over the temperature range 283.15 - 333.15 K using a KD2 Pro Thermal Properties Analyser (Pullman, USA). All the samples have been fully immersed in a Polyscience 9510 (Illinois, USA) thermostatic bath in order to ensure the temperature uniformity, as was also explained in Cabaleiro et al. [26]. The operating standard of KD2 Pro equipment is based on the Transient Hot-Wire (THW) method, that is extensively used for nanofluids measurement [13, 28] and the sensor behavior can be approximated with the simplified equation by Carslaw and Jaeger through the time temperature difference [26]. The accuracy of measurements was estimated as 3% [26, 29].

3. Results and discussions

3.1. pH results

The aggregation and sedimentation play an important role in the nanofluids stability and subsequently in their behavior as heat transfer agents. A number of studies indicated that the pH of the dispersion influence the overall stability of nanofluids [31-34]. Dispersions with high zeta potential (negative or positive) are electrically stabilized while dispersions with low zeta potentials tend to coagulate or flocculate [35, 36]. Moreover, it would be desirable that stable nanofluids present pH around centered values because very high or low value of pH may damage the heat transfer surface due to corrosion especially at high temperature [34].

The pH was measured at ambient temperature and the results are in Table 3. The pH of the dispersions was determined as around 8.0 - 8.5 as one can see in this table. The obtained pH values are in line with research performed by Wang and Li [37] who recommend an optimized value of pH = 8 for suspensions containing alumina with weight fraction up to 0.5, thus no surfactant was needed to be added.

Table 3. Results for pH for 0.25W+0.75IL mixture with different weight concentrations of Al_2O_3 nanoparticles

Fluid	pH
1% wt Al_2O_3 /(0.25W+0.75IL)	7.93
2.5% wt Al_2O_3 /(0.25W+0.75IL)	8.11
5% wt Al_2O_3 /(0.25W+0.75IL)	8.29
10% wt Al_2O_3 /(0.25W+0.75IL)	8.21
15% wt Al_2O_3 /(0.25W+0.75IL)	8.67

3.2. Density results

Densities were measured in the temperature range 283.15 - 313.15 K on samples around 1 ml volume and after each measurement, the device was properly cleaned. In addition, we performed firstly a calibration in order to ensure the best results accuracy and the experiment started with water and ionic liquid tests, as one can see in Table 4.

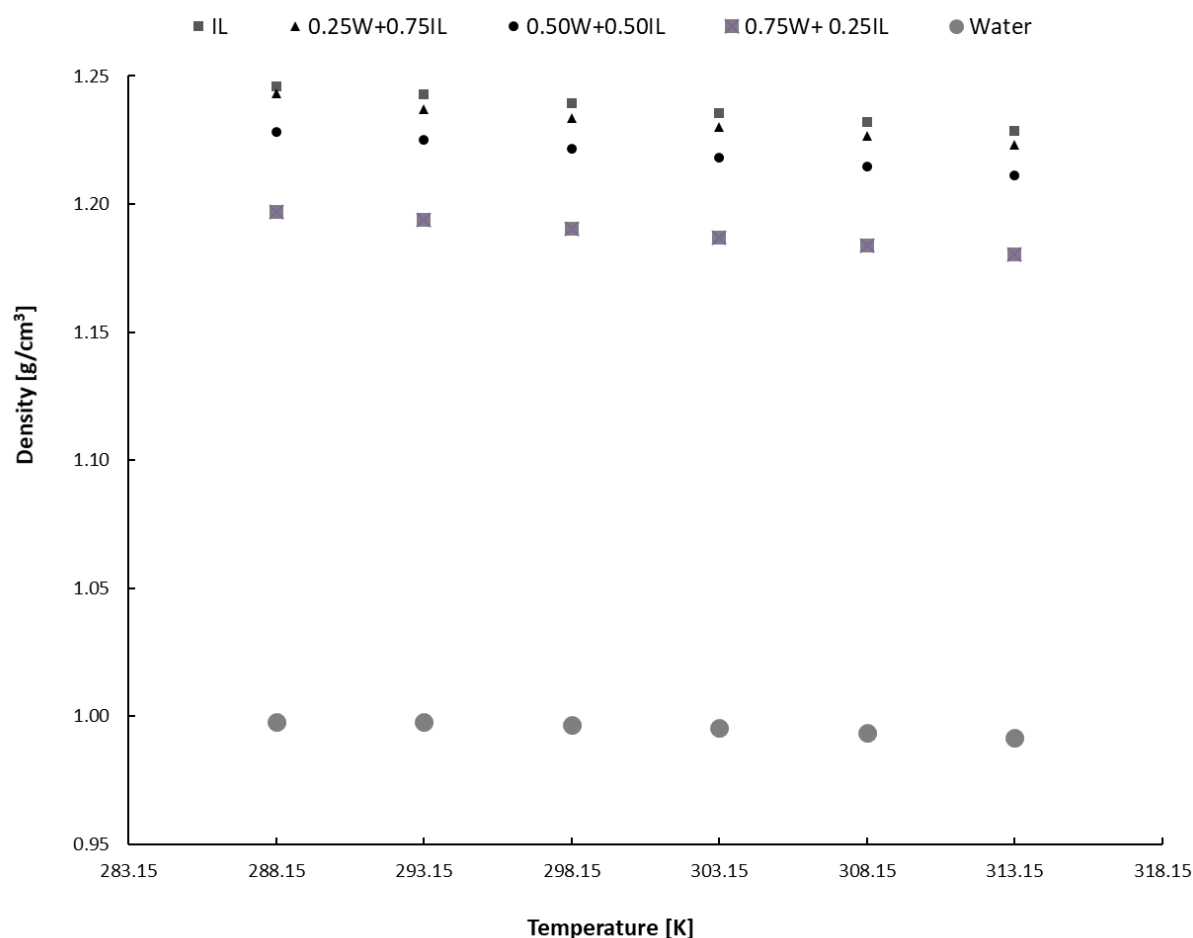
Table 4. Density results for the $[\text{C}_2\text{mim}][\text{CH}_3\text{SO}_3]$ ionic liquid

T [K]	Density, ρ [g/cm^3]	
	Bioucas et al. [24]	Current experimental study
288.15	-	1.2467
293.15	1.2452	1.2434
298.15	1.2417	1.2400
303.15	1.2383	1.2365
308.15	1.2348	1.2331
313.15	1.2314	1.2298

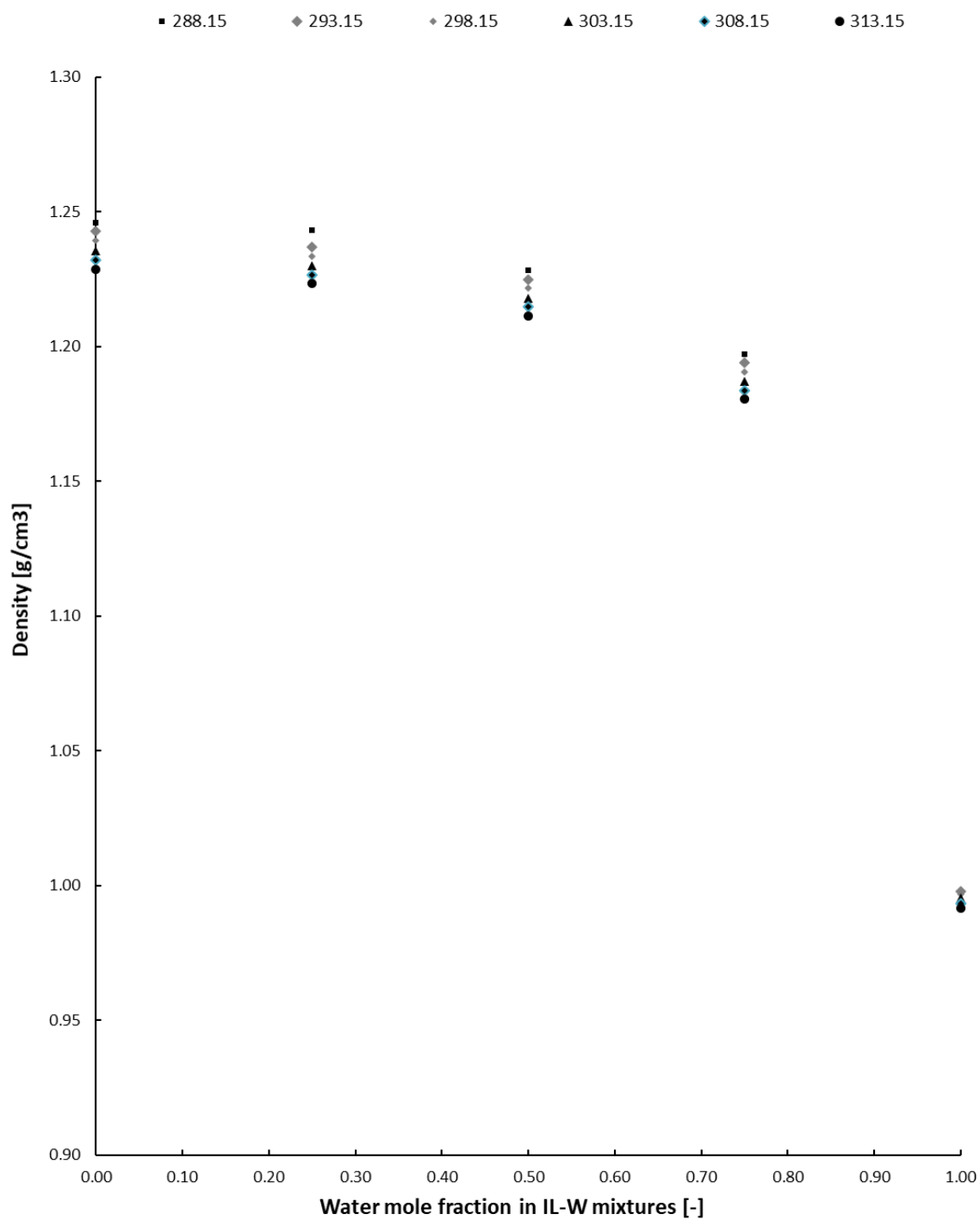
The results were compared with literature [24] and agreement was noticed in the range of 0.1% deviation. Generally, our experimental results are situated at about 0.1% lower than that of Bioucas et al. [24] and an explanation can rely on the fact that we used a slightly higher quantity of water for the samples or simply because of experimental uncertainty for both measurements.

Figure 3 depicts the variation with temperature of the mixtures density and one can see that density is slightly decreasing with the temperature increase while adding water to the base fluid goes to an almost linear decrease in the ionic liquid density for water mole fractions up to 0.75; with further addition of water molecules, density started a dramatically decrease until

reaching pure water values, as can be clearly seen from Figure 3b. This abrupt decrease in density at higher water mole fractions upon 0.75 could be due to the transition between an “IL-type” structure and a “water-type”, changing the molecular interactions between both components of the mixture [8, 25].



a.



b.

Figure 3. Density variation with temperature (a) and water mole fraction (b) for IL-water mixtures

Figure 4 presents in 3D the overall variation of density with temperature and water mole fraction. As can be observed in Figure 4, there is a strong influence of adding water on density decreasing, while temperature influence on the mixture density is rather weak. This influence appears at higher molar fractions of water as reported by Stark et al. [25].

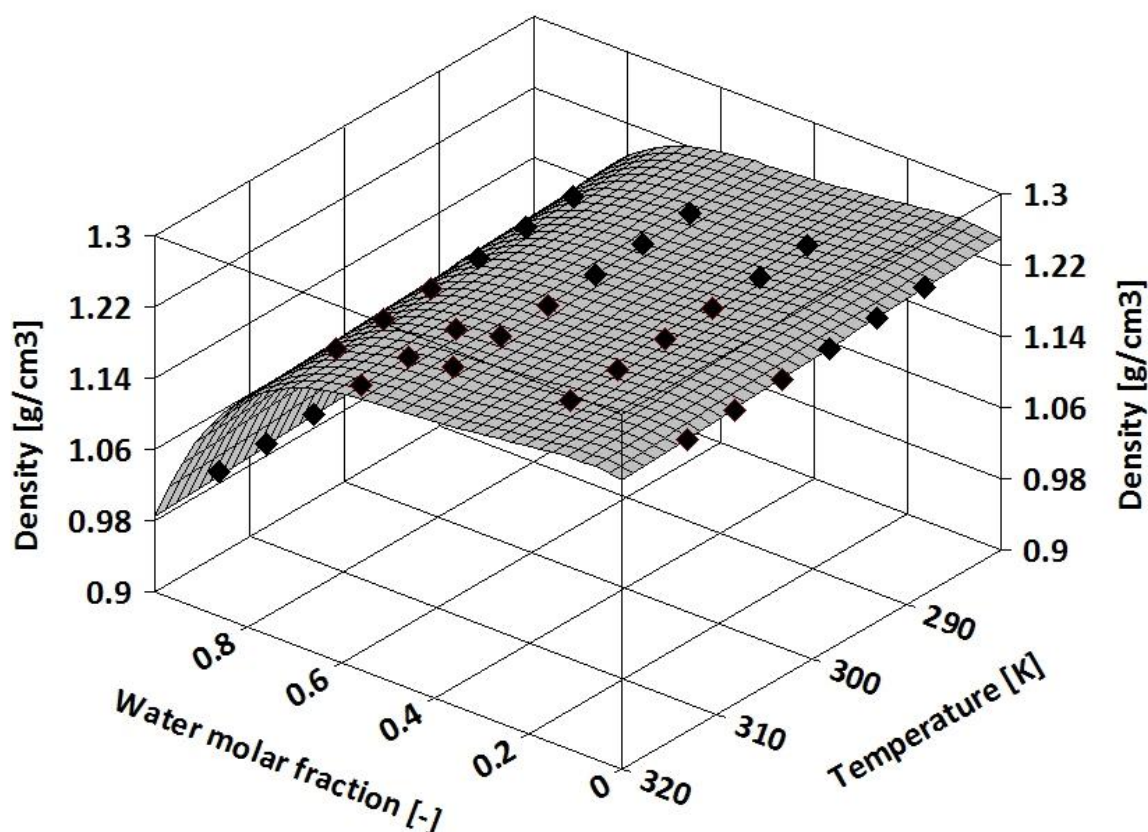


Figure 4. 3D analysis on density of IL-water mixtures

In conclusion, while the overall $[\text{C}_2\text{mim}][\text{CH}_3\text{SO}_3]$ density is higher by 25% than that of water, the influence of IL density over the mixtures is much higher than that of water. More precisely, adding water to the IL decreases the mixture density by 0.45%, 1.4% and 3.9% depending on water mole fraction (0.25, 0.50 and 0.75, respectively), while density variation with temperature is low (approximately 1 % for an overall value of 40 degrees' variation).

Figure 5 and Figure 6 show the variation of density over the temperature for the two studied dispersions: IL and 0.25W+0.75IL mixtures plus alumina nanoparticles in weight

concentrations between 0-5%. One can notice here that overall, the density is decreasing with temperature both for IL and 0.25W+0.75IL dispersions while the density is increasing after dispersing nanoparticles to the mixtures.

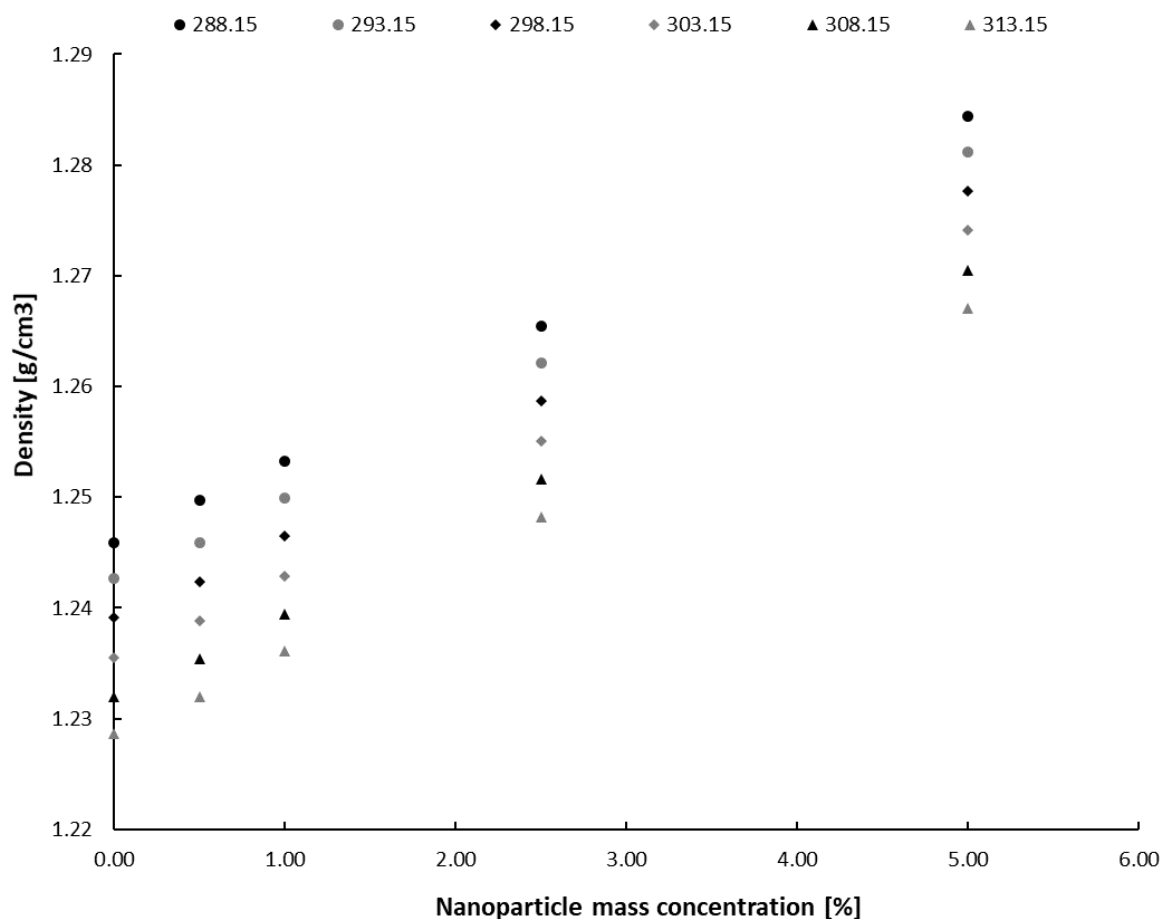


Figure 5. Density variation over temperature for NEILs (dispersion of alumina into pure ionic liquid)

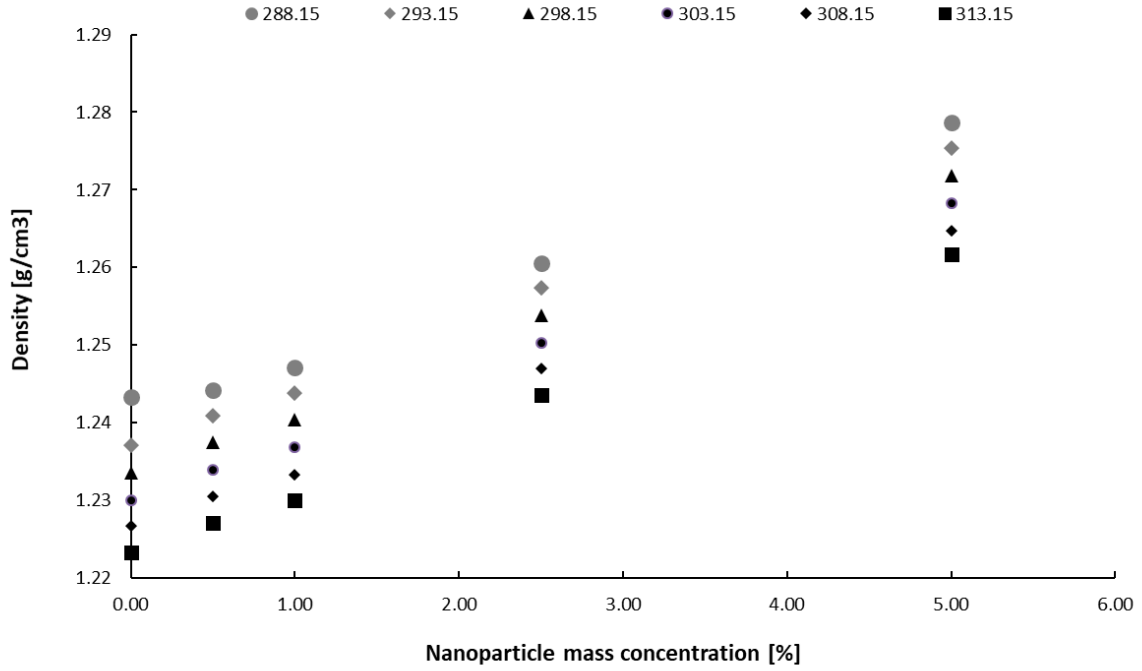


Figure 6. Density variation over temperature for NEILs: dispersions of alumina into 0.25IL +0.75 W mixture

Furthermore, a comparison with the equation used for nanofluids density evaluation was performed and results are in Table 5. The evaluation is in percentages difference between experimental and theoretical values and one can notice that the theoretical values are in perfect agreement with the experiment, differences being less than 1% (i.e.: more exactly in the range 0.01 – 0.92 %). Data from Table 5 were calculated considering a constant density of the alumina nanoparticles in the temperature interval 288.15-313.15 K and a variable density with temperature for the base fluids.

The density equation is proposed by Pak and Cho [38]:

$$\rho_{\text{inf}} = \varphi_{\text{vol}} \rho_p + (1 - \varphi_{\text{vol}}) \rho_{\text{bf}} \quad (3)$$

where the used nanoparticle density is 4.00 g/cm³, as reported by the manufacturer, and the volume fractions were calculated at each experimental temperature using the mass fraction, according to [39]:

$$\frac{1}{\phi_{\text{vol}}} = 1 + \frac{\rho_p}{\rho_{\text{bf}}} \left(\frac{1 - \phi_{\text{wt}}}{\phi_{\text{wt}}} \right) \quad (4)$$

Table 5. Differences between experimental and theoretical values, in %

Fluid	Temperature [K]	Alumina mass concentration [%]			
		0.5	1.0	2.5	5.0
IL	288.15	0.49	0.60	0.59	0.95
	293.15	0.50	0.61	0.59	0.95
	298.15	0.49	0.60	0.59	0.97
	303.15	0.48	0.60	0.59	0.97
	308.15	0.48	0.61	0.59	0.98
	313.15	0.48	0.61	0.59	0.96
0.25W+0.75IL	288.15	-0.17	-0.10	0.00	0.30
	293.15	-0.35	-0.33	-0.24	0.08
	298.15	-0.36	-0.33	-0.23	0.08
	303.15	-0.36	-0.33	-0.23	0.09
	308.15	-0.36	-0.32	-0.22	0.11
	313.15	-0.35	-0.32	-0.21	0.12

3.3. Thermal conductivity results

Thermal conductivity was experimentally determined for binary mixtures identified in Table 2, as well as for NEILs by using two base fluids (i.e. IL and 0.25W+0.75IL) in the temperature interval 283.15 – 333.15 K.

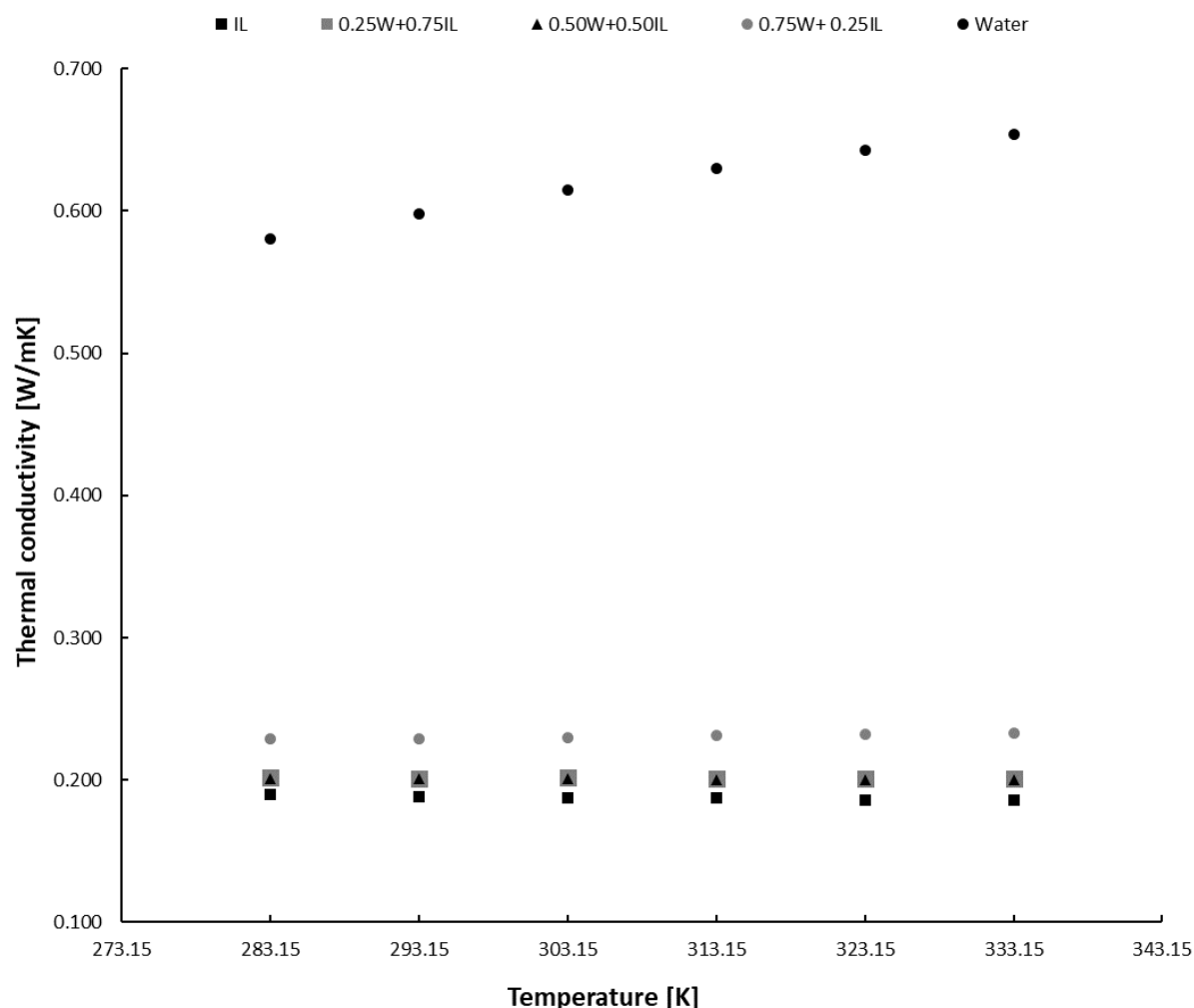


Figure 7. Thermal conductivity versus temperature for IL-W mixtures

Results are depicted in Figure 7 for all binary mixtures and it can be noticed an increase in thermal conductivity of the mixture while adding water to ionic liquid in different mole fractions. Nevertheless, the beneficial effect on thermal conductivity is obvious, while the water thermal conductivity is more than 3 times higher than that of the ionic liquid.

Moreover, in Figure 8 it can see the variation of thermal conductivity with water mole fraction at ambient temperature and it can be noticed the influence of water in the thermal conductivity of the mixture. Actually, this influence is around 7% for water mole fraction of 0.25 and 0.5 and increases at 23% for a mole fraction of 0.75. In the same way as density,

thermal conductivity remained almost constant until reached water mole fraction of 0.75, when the addition of more water in the mixture leads to a high increase in the thermal conductivity [8, 25].

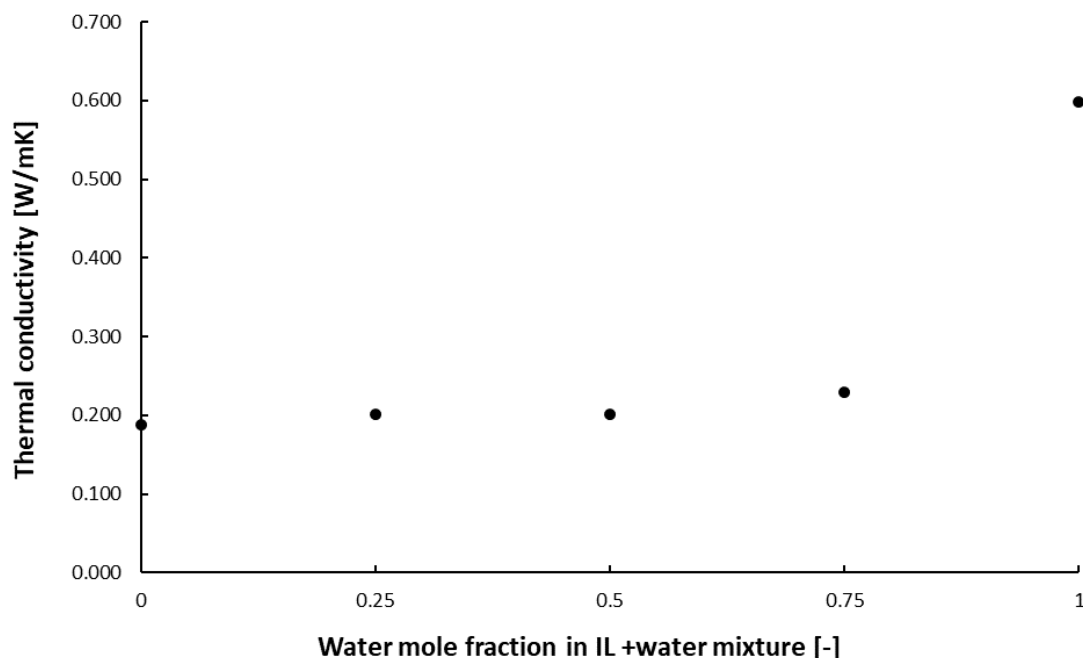


Figure 8. Thermal conductivity for all mixtures ionic liquid + water at 293.15K

When nanoparticles are dispersed conveniently into the base fluids, thermal conductivity increases with the weight concentration of alumina nanoparticles, as one can see from Figure 9. Thermal conductivity of dispersions is enhanced up to 13 % by adding very small concentrations of alumina nanoparticles, while it remains almost constant with temperature rising. More exactly, for the 15% wt $\text{Al}_2\text{O}_3/\text{IL}$ alumina at 20 °C, the thermal conductivity is increased by 12.9% if compared with IL. In addition, the same trend was noticed for dispersions with ionic liquid and water as base fluid, as can be seen from Figure 9.

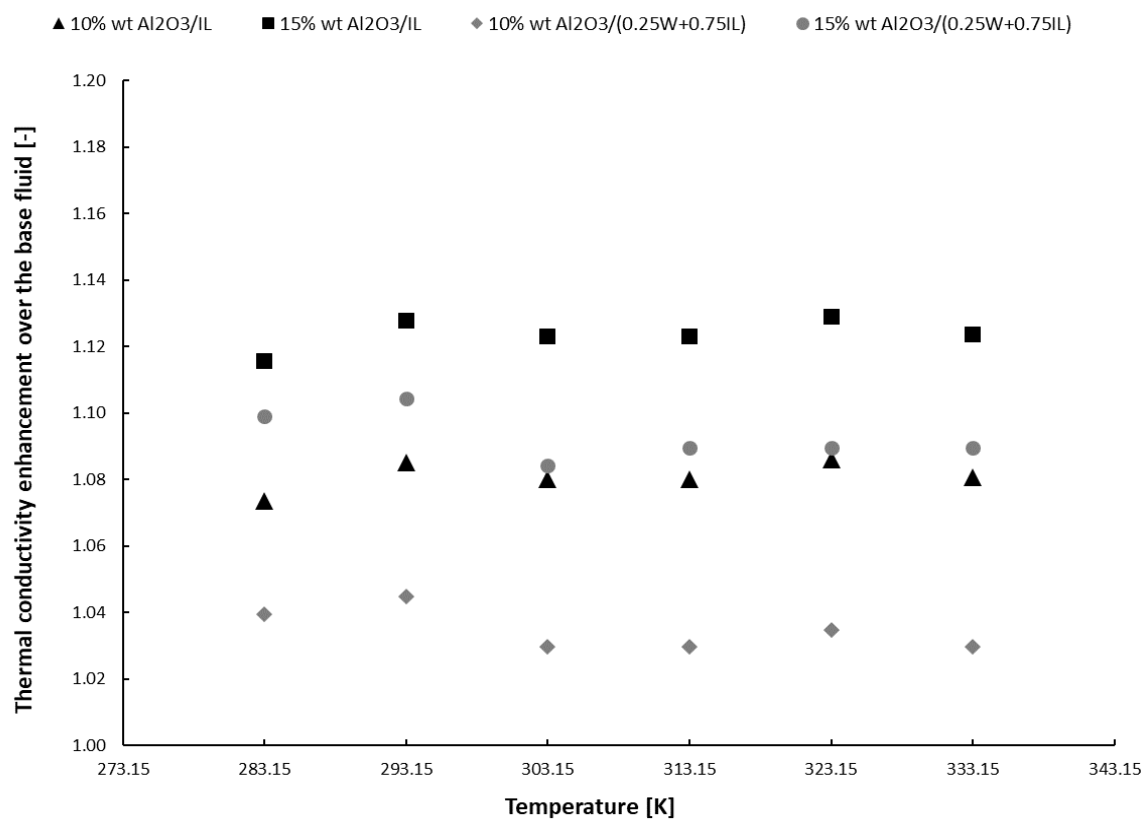


Figure 9. Thermal conductivity enhancement over the base fluid for the dispersions

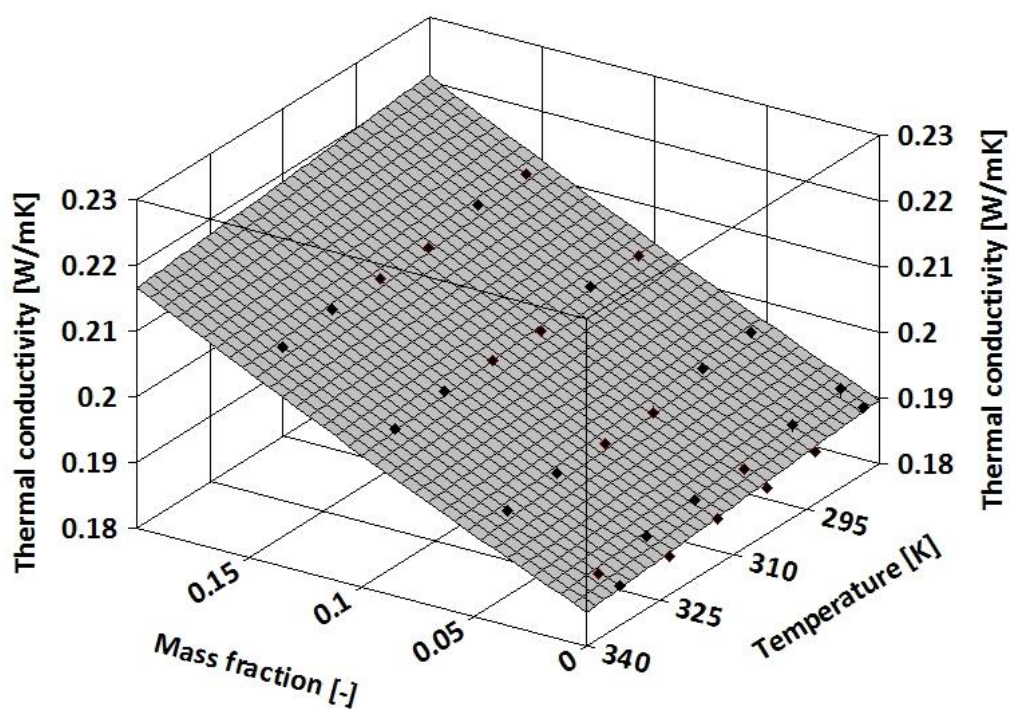


Figure 10. 3D analysis on thermal conductivity of NEILs: dispersion of alumina into pure ionic liquid

At a more complex analysis of ionic liquid based ionanofluids (NEILs) with Table Curve 3D software [40] it can get:

$$k_{\text{inf}} = 0.210 + 0.114\phi_{\text{wt}} + 0.082\phi_{\text{wt}}^2 - 7.3143 \cdot 10^{-5}T \quad (5)$$

where k is the thermal conductivity, ϕ_{wt} is the mass fraction of alumina nanoparticles and T is temperature in K. Eq. (5) is plotted in Figure 10 and has an R squared value of 0.996.

It can be seen in Figure 10 the strong influence of adding nanoparticles to IL on thermal conductivity, while temperature influence is rather fragile, as was noticed also from Figure 9a. Plus, it can clearly say that the addition of nanoparticles goes to an increase in dispersions thermal conductivity of 1-13 % depending on the alumina mass concentration, if compared with the base fluid.

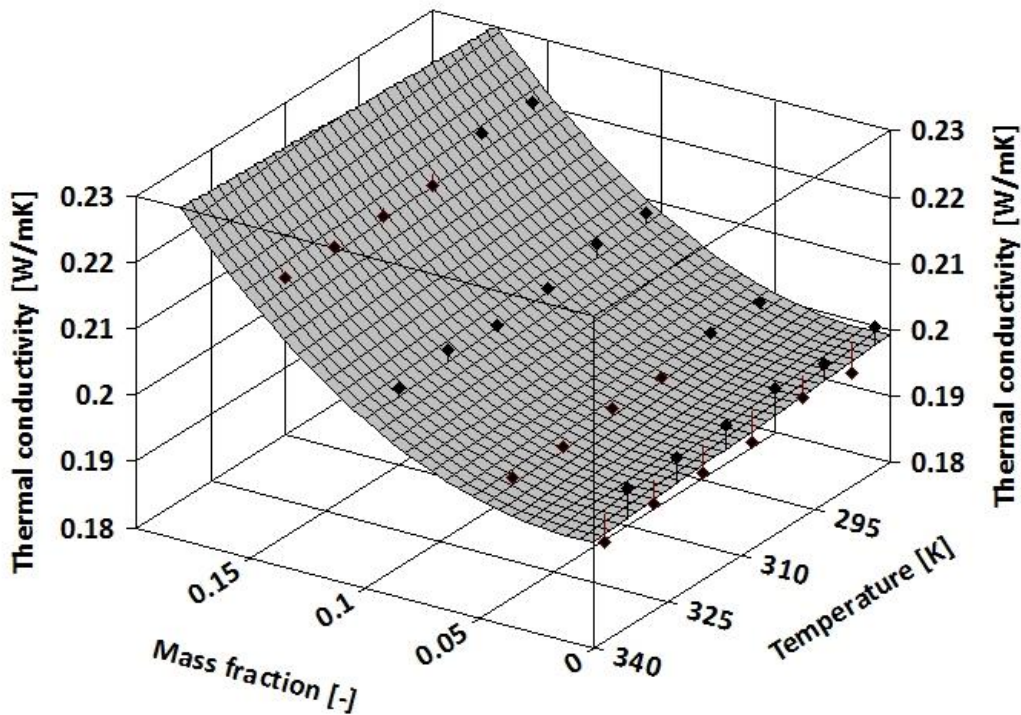


Figure 11. 3D analysis on thermal conductivity of NEILs: dispersion of alumina into 0.25W+0.75IL

If 0.25W+0.75IL is considered as base fluid, in Figure 11 is the 3D analysis while the proposed correlation is:

$$k_{inf} = 0.214 + 0.025\phi_{wt} + 1.179\phi_{wt}^2 - 5.257 \cdot 10^{-5}T \quad (6)$$

where k is the thermal conductivity, ϕ_{wt} is the mass fraction of alumina nanoparticles and T is temperature in K. Eq. (6) has an R squared value $R^2 = 0.916$.

On the other hand, the Maxwell theoretical equation [41] is widely used in the literature and offers trustable results for low particle loading, as was affirmed in the Round Robin tests on thermal conductivity performed by Buongiorno et al. [42] and is expressed as:

$$\frac{k_{inf}}{k_{bf}} = \frac{k_p + 2k_{bf} + 2\phi_{vol}(k_p - k_{bf})}{k_p + 2k_{bf} - \phi_{vol}(k_p - k_{bf})} \quad (7)$$

Additionally, a comparison with the theoretical formula proposed by Maxwell [41] used for nanofluids thermal conductivity evaluation was performed and results are in Figure 12. The evaluation is in percentages difference between experimental and theoretical values and one can see that the theoretical values are in good agreement with the experiment, differences being about $\pm 4\%$. Nevertheless, Maxwell equation is perfectly fitting the experimental data for the ionic liquid-based nanofluids while for the IL+water-based dispersion the deviation goes to almost 7%. In almost all cases, the Maxwell model is slightly under-predicting the experimental values, but can be a good tool to estimate the thermal conductivity of nanoparticles enhanced ionic liquids when experimental data are not available.

The nanoparticle thermal conductivity used for theoretical evaluation was 40 W/m K [39] and the volume fractions were calculated at each experimental temperature using the mass fraction, according to eq. (4).

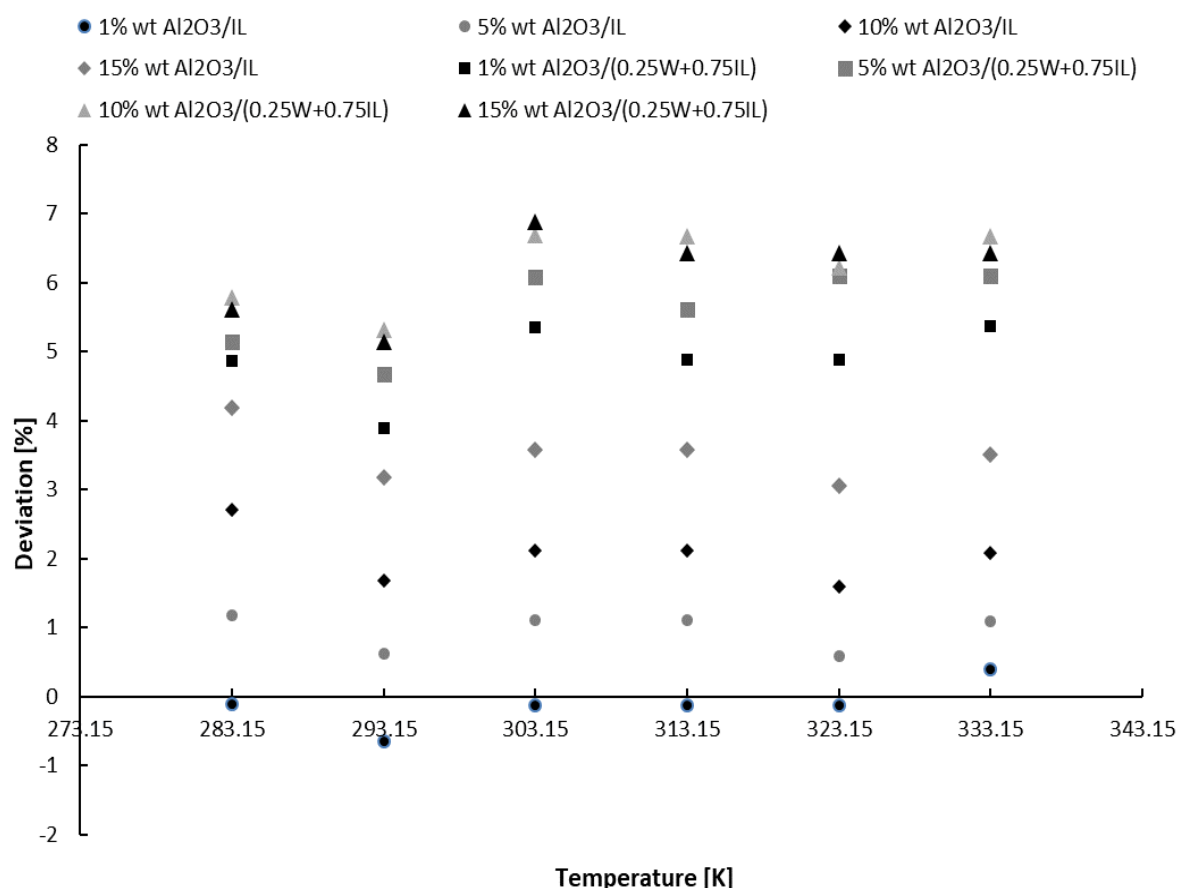


Figure 12. Deviation in thermal conductivity between experimental and Maxwell correlation

4. Conclusion

This study involves a complex experimental evaluation of a less studied ionic liquid, $[C_2mim][CH_3SO_3]$, while adding water, and alumina nanoparticles are dispersed. Three mixtures were manufactured by mixing water with IL in three molar fractions and then nanoparticles were dispersed thus resulting NEILs. The new nanofluids stability was very good as the pH results are satisfactory thus, no surfactant was needed.

Overall, this study reveals a certain enhancement of NEILs thermal conductivity ($<12.9\%$) and the specific heat and density varies according to well-known correlations. This study added value can be synthesized as:

- density was found to be in line with existing equations and a new correlation was proposed;

- thermal conductivity is increasing when nanoparticle mass fraction increase;
- new correlations based on temperature and mass fraction variation for NEILs thermal conductivity estimation were proposed.

As a general conclusion, the $[C_2mim][CH_3SO_3]$ ionic liquid and corresponding NEILs can be seen as a possible candidate for heat transfer application even if its study have to be continued with other properties evaluation and further on, with its implementation in a real case scenario.

Acknowledgments

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Highlights

- ionic liquid-water mixtures were prepared
- pH of developed new fluids is measured and good stability is noticed
- Al_2O_3 NEIL density is experimentally examined and good agreement with existing equations was noticed
- Al_2O_3 NEIL thermal conductivity is experimentally examined and an enhancement was noted
- Al_2O_3 NEIL thermal conductivity correlations are proposed

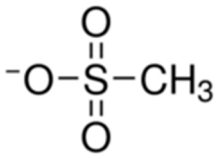
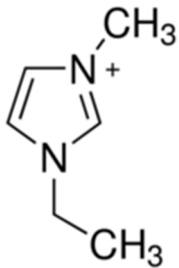


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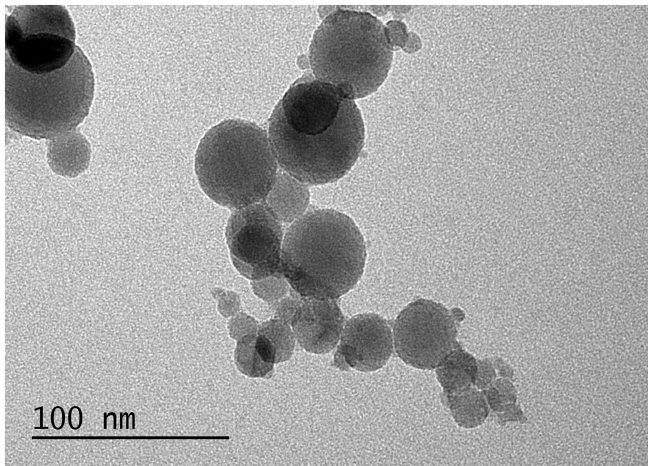


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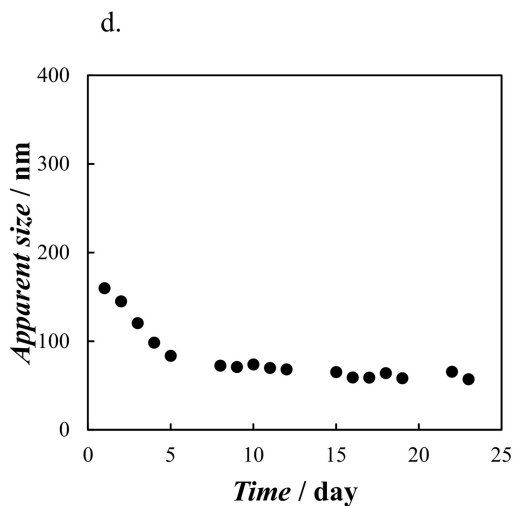
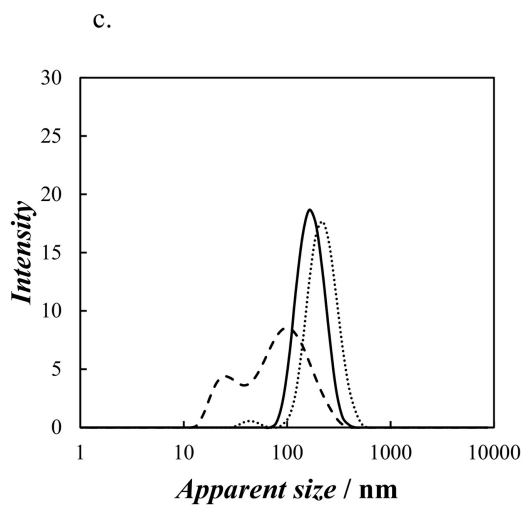
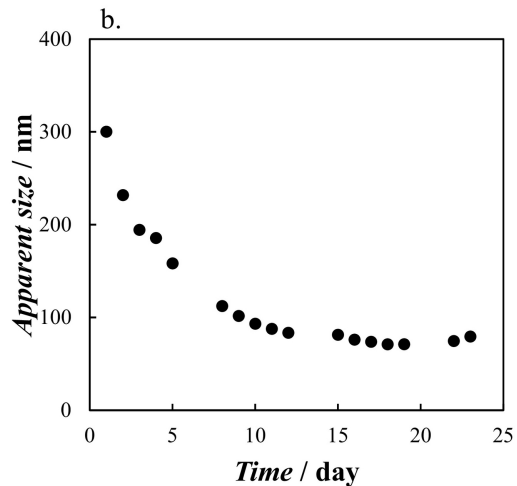
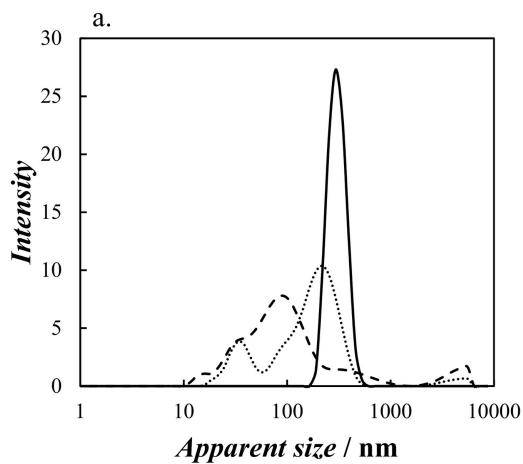
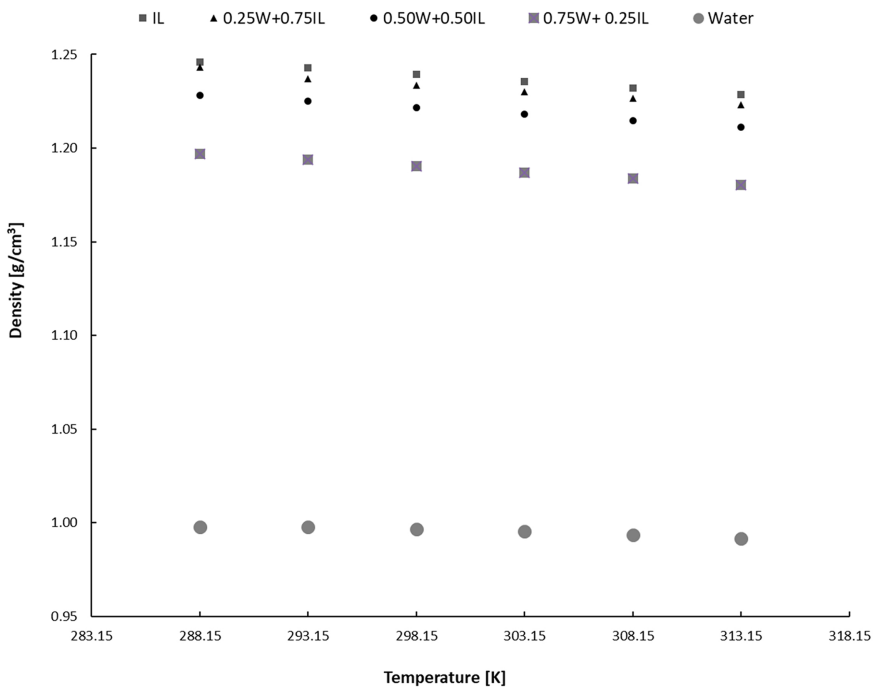
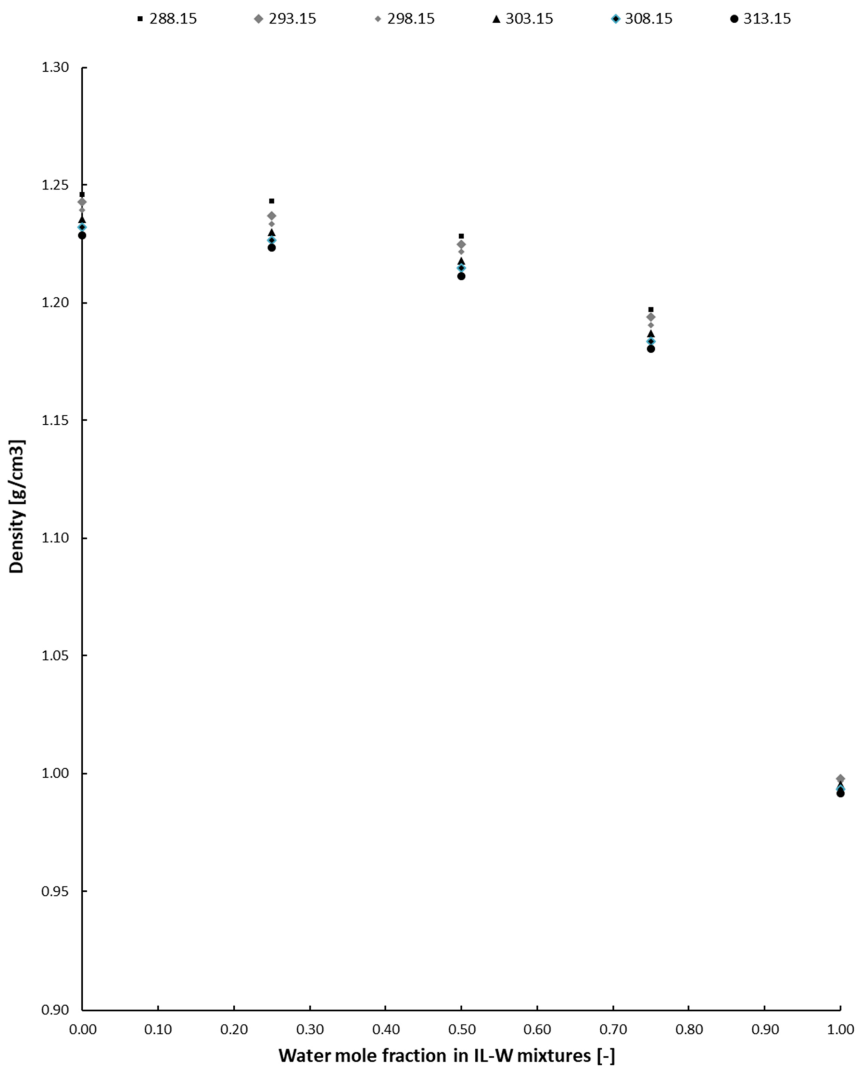


Figure 3



a.



b.

Figure 4

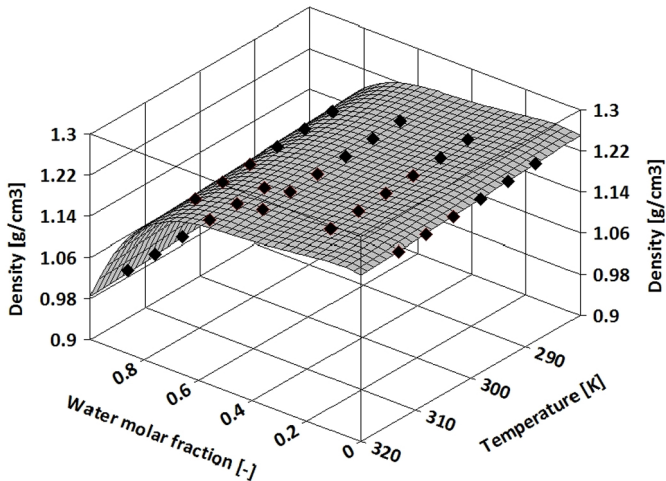


Figure 5

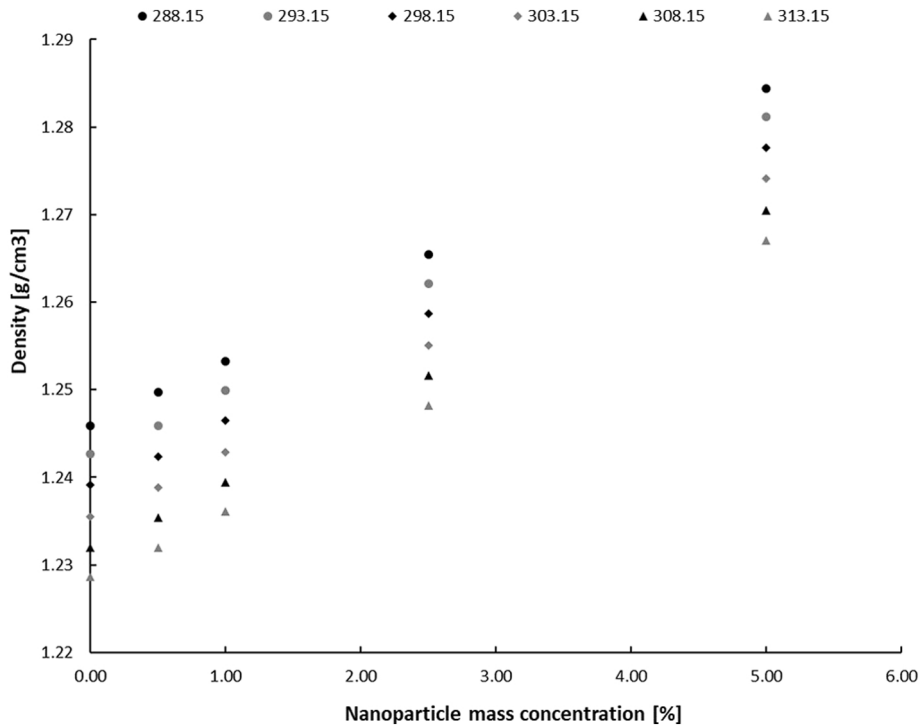


Figure 6

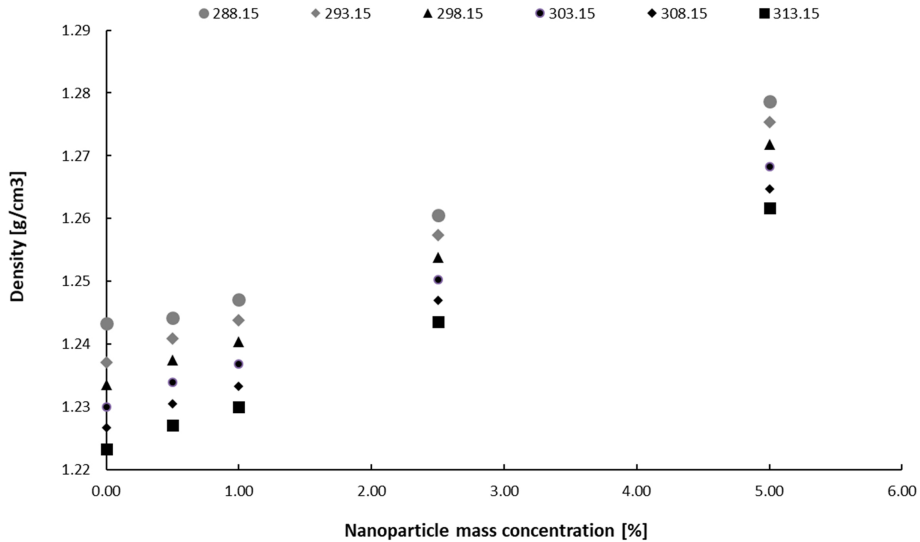


Figure 7

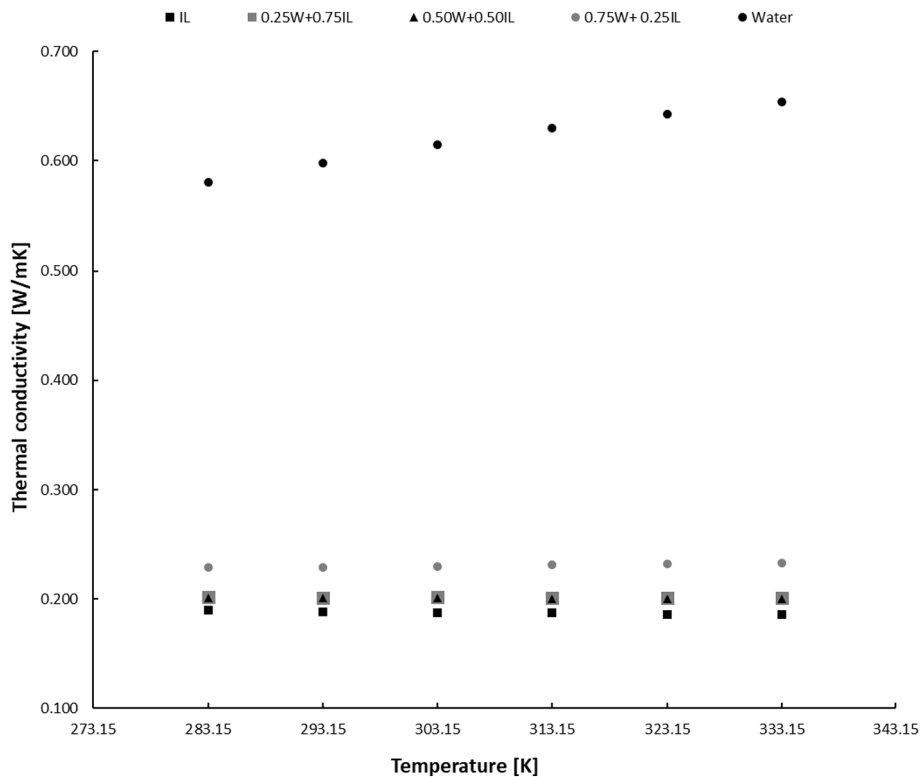


Figure 8

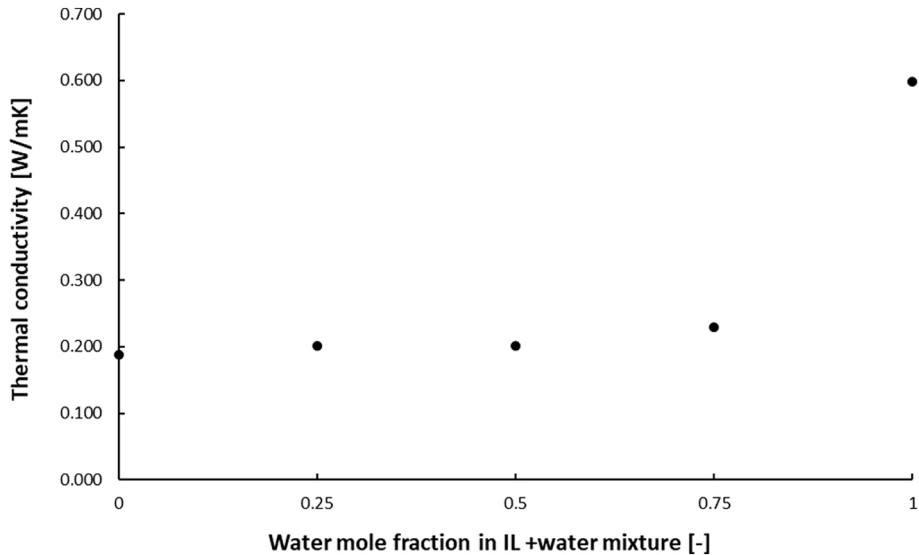


Figure 9

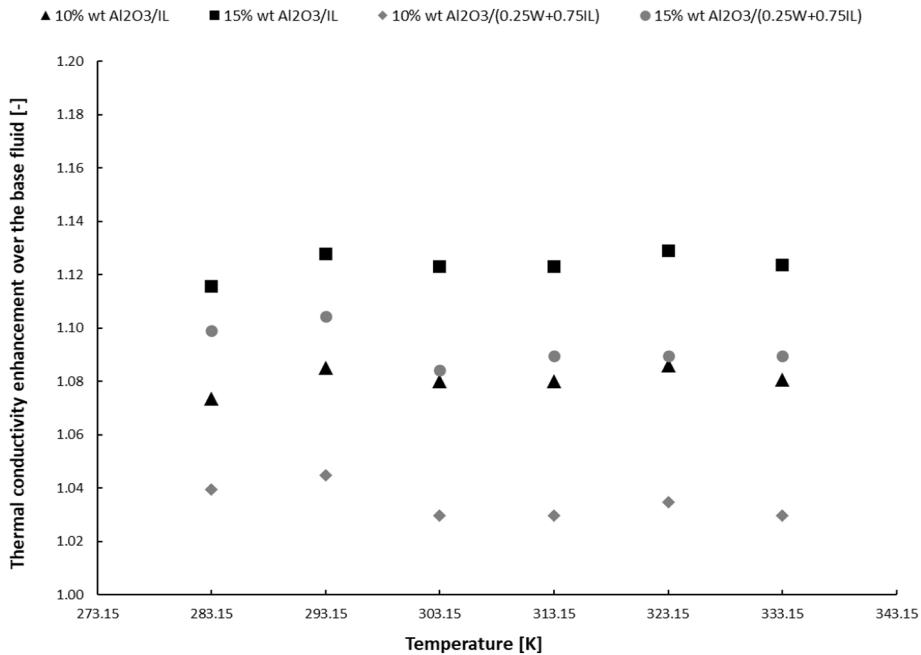


Figure 10

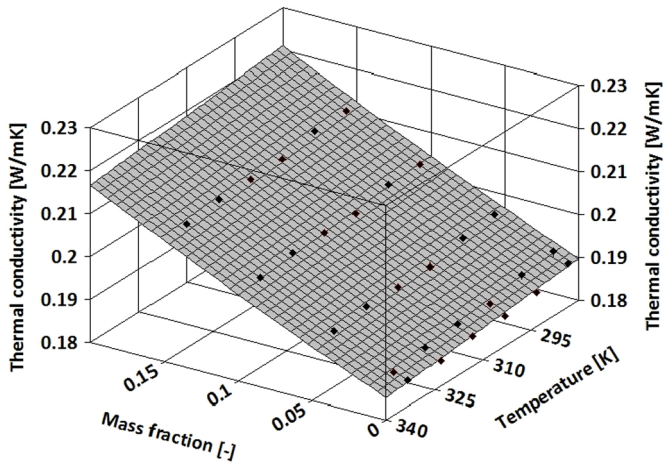


Figure 11

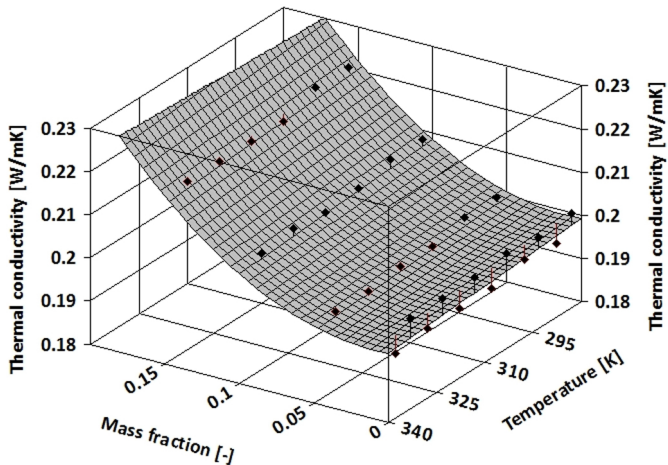


Figure 12

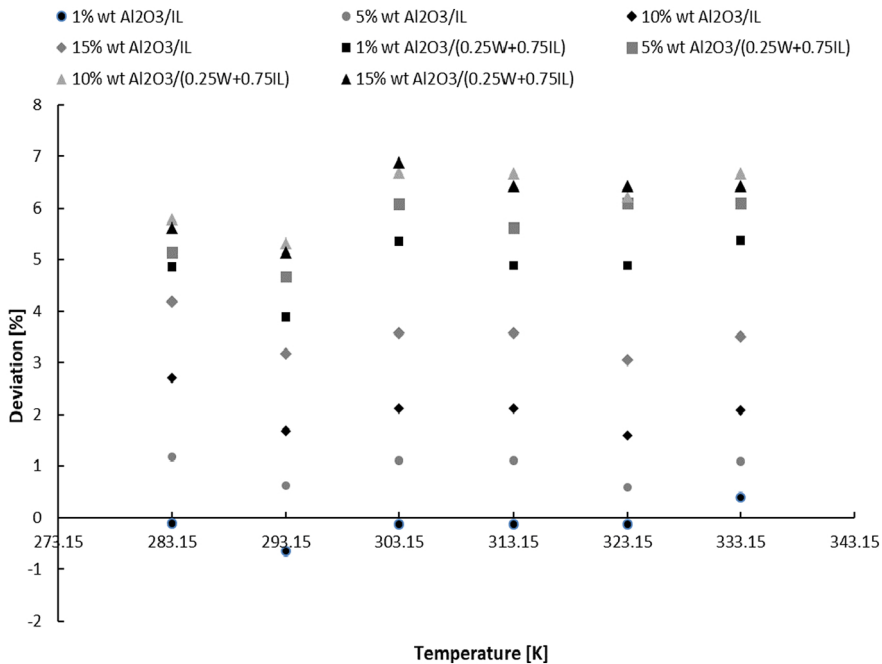


Figure 13