



Thermophysical properties of ionic liquid dicyanamide (DCA) nanosystems



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Dedicated to the memory of the late Professor Manuel Ribeiro da Silva.

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ABSTRACT

IoNanofluids have emerged as a possible alternative to current engineering fluids for heat transfer applications, namely in small volume heat exchangers and micro-channels. Thermal conductivity and density play a crucial role for the chemical plant design of green processes. Existing data are very scarce and inaccurate, mostly affected by impurities and the presence of water in the ionic liquids.

In the present paper, we report new data on the thermal conductivity and density of 1-*n*-butyl-3-methyl-imidazolium dicyanamide ([C₄mim][dca]), 1-ethyl-3-methyl-imidazolium dicyanamide ([C₂mim][dca]) and 1-butyl-1-methyl-pyrrolidinium dicyanamide ([C₄mpyr][dca]) at temperatures between (293 and 343) K at *p* = 0.1 MPa and IoNanofluids based on them with MWCNTs (multi-walled carbon nanotubes), in order to understand the effect of adding nanomaterials to a ionic liquid matrix and its modification of the heat transfer mechanism. Discussion about the effect of the cation, its side alkyl chain, head group and anion structure in the properties studied concluded that it is essential to understand better the mechanism of heat transfer in these systems, namely the role played by the interface ionic liquid (cation and anion)-nanoparticle, whatever molecular shape they have. Current theories used to calculate the thermal conductivity enhancement are insufficient to predict its value and variation with volume fraction of the nanomaterial.

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1. Introduction

In a time where the environmental awareness and the optimization of current energy technologies are so evidently emphasized, the unique characteristics of ionic liquids have drawn the attention of chemical companies and scientific community over recent years. The potential displayed by these fluids reveals applicability in several areas of modern chemistry, from analytical chemistry to catalysis and from petrochemical industry to nuclear industry. Furthermore, these substances promise some benefits regarding the preservation of the environment, stimulating the practice of the philosophy of green chemistry [1,2]. In the field of heat transfer, there is a need for new heat transfer fluids, capable of replacing environmentally harmful existing ones with properties that can result in maximum possible energy efficiency, in order to support healthy and sustainable applications, either domestic and/or industrial.

Nanomaterials and nanotechnology are a considerable part of the daily discussions on our society, revealing an ability to revolutionize modern life within various fields from engineering to medicine. The main objective of current research is to minimize the volume of any material used, maintaining or upgrading the efficiency of the latter and to support a healthy economy. Modern nanotechnology can generate metallic or non-metallic particles and structures with distinct mechanical, optical, magnetic, electrical, chemical and thermal properties [3]. Once stably suspended in a fluid, these particles can greatly enhance the properties of the host fluid, becoming a nanofluid [4].

Ionic liquids have been studied as possible heat transfer fluids due to their high volumetric heat capacity and good thermal conductivity [5] and the combination of nanomaterials with these fluids creates great expectation considering the enhancement of their thermophysical properties. Recent work on this area has been accomplished by Nieto de Castro *et al.* [6–10] successfully measuring the thermal conductivity and heat capacity of mainly imidazolium based ionic liquids with suspended multi-walled carbon nanotubes (MWCNTs) as a function of temperature, giving rise to

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the term IoNanofluids. The use of nanoparticles as enhancing agents of the fluids properties enables the association of little quantities of different nanoparticles with different ionic liquids, thus obtaining flexible and designable (on a molecular level) substances that can be conceived according to the properties needed for a certain application. In what concerns heat transfer, the fluid chosen for such a task should possess fluidity in order to be able to flow through the tubes of, for example, a shell and tube heat exchanger, or any other heat transfer unit. On the other hand, the fluidity of the suspension of nanoparticles will depend on the method used to attain the suspension itself. Considering the work of Aida and Fukushima [11,12], the use of “bucky gels” (there described as gelatinous, soft composite materials) in such an application would be somewhat limited, due to the lack of fluidity on part of these suspensions. In our latest work [10], the IoNanofluids based on $[\text{C}_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ and $[\text{C}_2\text{mim}][\text{EtSO}_4]$ could be described as slightly-to-moderate viscous fluids, i.e., possessing considerable fluidity. As should be expected, the addition of nanomaterials to an ionic liquid should lead to an increase of the viscosity of the resulting IoNanofluid. Hence, if the starting point of the IoNanofluid were to be an ionic liquid with lower viscosity, the end result should be a fluid with a more adequate viscosity and, consequently, a more suitable performance on the aforementioned application. When comparing the viscosity values of the ionic liquids studied in reference [10,13,14] with the imidazolium dicyanamide ionic liquids here presented [15,16] at $T = 298.15\text{ K}$ and 0.1 MPa , one can assess that the dicyanamide ionic liquids can have lower viscosity values that can range from $(0.02\text{ to }0.074)\text{ Pa}\cdot\text{s}$. Thus, these ionic liquids may well be an optimum starting point considering the use of IoNanofluids as heat transfer fluids [5,8,10].

This work reports thermal conductivity and density measurements of 1-*n*-butyl-3-methyl-imidazolium dicyanamide ($[\text{C}_4\text{mim}][\text{dca}]$), 1-ethyl-3-methyl-imidazolium dicyanamide ($[\text{C}_2\text{mim}][\text{dca}]$) and 1-butyl-1-methyl-pyrrolidinium dicyanamide ($[\text{C}_4\text{mpyr}][\text{dca}]$) at temperatures between $(293\text{ and }343)\text{ K}$ at 0.1 MPa and IoNanofluids based on them with MWCNTs. It also compares the obtained results with current theories of thermal conductivity enhancement in nanofluids.

2. Materials and methods

2.1. Materials

All three ionic liquids were purchased from IoLiTec, Ionic Liquids Technologies, Germany, and the product specifications of the certificate analysis can be found in table 1. The estimated mass fraction purity is 0.98 or better. As usual in the ionic liquids supplied by this company, the unusual colour of the liquids is due to the presence (below 2%) of the corresponding bromide precursor since it is common for these liquids to be synthesized with a chloride precursor and therefore, usually, remain colourless. The water content was confirmed using Coulometric Karl Fischer titration (Metrohm 831) and, being considerable to create an effect on the

thermal conductivity [10], further purification was performed through drying the ionic liquids around $T = 333\text{ K}$, under vacuum, for a minimum period of 48 h. As the presence of water changes considerably the properties of the ionic liquids, its content was analyzed before and after the experimental measurements. Measurements were made at atmospheric pressure. Taking into account its variation in the laboratory during the measurement period, the values are reported to $0.1\text{ MPa} \pm 1\text{ kPa}$, the uncertainty being estimated by the maximum daily variation in the barometric pressure in the laboratory.

The carbon nanotubes used were multi-walled carbon nanotubes Baytubes C150 HP (MWCNTs) from Bayer Material Science, a development product that has been previously used by our group [6], and whose characteristics are displayed in table 2.

2.2. Equipment and methodology

2.2.1. Thermal conductivity

Thermal conductivity was measured using the KD2 Pro™ Thermal Properties Analyzer (Decagon Devices, Inc.). The principle of measurement is based on the transient hot-wire method (THW) using a single-needle sensor (1.3 mm diameter and 60 mm long). This sensor contains a heating element and a thermal resistor, which should be inserted vertically in the sample to assure that free convection, is minimized. The measurement is accomplished through the heating of the sensor (inserted in the sample) at a certain rate while simultaneously monitoring the temperature variation. All this is controlled by a microprocessor connected to the sensor that also calculates the thermal conductivity of the sample based on a parameter-based corrected version of the temperature model given by Carslaw and Jaeger for an infinite line heat source with constant heat output and zero mass in an infinite medium [17]. Further information on these calculations can be found elsewhere [6,18]. Each measured sample had an approximate volume of 85 cm^3 to ensure that the dimensional requirements of the sensor were matched, since it was specified in the device's manual that a minimum amount of material should be present in all directions. With the sensor inserted vertically, the glass vial was then suspended (not inserted, in order to avoid the vibrations of the bath that could induce convection) in a temperature-controlled oil bath (Haake C25; oil – Galp Electric 2) and allowed to stabilize the temperature for each sample measured. The time to reach the desired temperature fluctuated with the sample being measured, as for the IoNanofluids it took longer because these fluids are more viscous and thick, therefore with smaller thermal diffusivity. Once attained the desired temperature, 8 to 10 measurements were taken with an interval of 15 min between each one to ensure reproducibility. Temperature was measured by a platinum resistance probe, part of the thermal conductivity probe, with an uncertainty $u(T) = 0.1\text{ K}$.

Calibration is an important part of any analytical procedure in the sense that it allows determining the extension of the deviation of the measured property of the substance being studied through the comparison/correspondence with the value of the same property of a known and rigorously studied standard. The procedure of the calibration for the thermal conductivity measurements presented on this work has been extensively described elsewhere [10]. In summary, the experimental thermal conductivity of substances such as water, toluene, glycerin, a mixture of glycerin and water (50/50 w/w) and an aqueous solution of NaCl was used to obtain a calibration constant, K , given by equation (1):

$$K = \frac{\lambda_{\text{meas}}}{\lambda_{\text{ref}}}, \quad (1)$$

based on the ratio between the experimental thermal conductivity (λ_{meas}) and a bibliographic reference (λ_{ref}) of the same property at

TABLE 1
Ionic liquids product specifications, purity as mass fraction.

Property	$[\text{C}_2\text{mim}][\text{dca}]$	$[\text{C}_4\text{mim}][\text{dca}]$	$[\text{C}_4\text{mpyr}][\text{dca}]$
Identity (NMR. IR)	Pass	Pass	Pass
Assay (NMR)	>0.98	>0.98	>0.98
Cation (IC)	0.987	0.992	0.999
Anion (IC)	0.989	0.985	0.995
Halides (IC)	<0.02	<0.02	<0.02
Water (KF)	$1850 \cdot 10^{-6}$	$1480 \cdot 10^{-6}$	$1710 \cdot 10^{-6}$
Appearance	Yellow liquid	Yellow liquid	Orange liquid
Date	02.02.2010	02.02.2011	02.02.2011

TABLE 2
Baytubes® C150 HP product specification.^a

Property	Value	Unit	Method
C-purity	>0.99	Mass fraction	Elementary analysis
Free amorphous carbon	Not detectable	Mass fraction	TEM
Number of walls	3 to 15		TEM
Outer mean diameter	13 to 16	nm	TEM
Outer diameter distribution	5 to 20	nm	TEM
Inner mean diameter	4	nm	TEM
Inner diameter distribution	2 to 6	nm	TEM
Length	1 to 10	μm	SEM
Bulk density	140 to 230	kg · m ⁻³	EN ISO 60

^a http://www.baytubes.com/product_production/baytubes_data.html.

the same temperature and pressure. This constant, liquid and temperature-independent, was found to have the value of (1.026 ± 0.034) , illustrating an overestimate (+2.6% relatively to the reference values) by the device, and leading to the correction of the experimental data. The values for the reference values of the calibrating fluids can be found in reference [10].

2.2.2. Density

Density measurements were carried out in a vibrating tube densimeter Anton Paar DMA 512P, at atmospheric pressure. The range of temperature was obtained with the aid of the above mentioned temperature-controlled oil bath and monitored with a calibrated platinum thermometer with an expanded uncertainty of $T = 0.05$ K, placed at the entrance of the measuring cell.

Actions were taken to ensure that all of the material and adjacent parts of the densimeter were well cleaned and dry before measuring the density of each sample. After cautiously injecting the sample in the cell (in order to avoid the formation of bubbles), the liquid was allowed to stabilize at the current temperature for at least 15 min. Once the thermal equilibrium was attained, the vibrating period was registered (at least 10 records) given that the variation of the value was negligible.

The calibration for the density measurements of the present work was accomplished using a one-fluid calibration method based on the work of Lampreia and Nieto de Castro [19]. Although the theory of the instrument is well known, its use is still object of less accurate applications. Therefore we describe briefly its application here.

The density ρ of a given sample depends on the period of vibration τ of the mechanical oscillator through equation (2):

$$\rho = A\tau^2 - B, \quad (2)$$

where A and B are instrument characteristics which are determined through the use of calibrating fluids of known density. The measurement principle of the instrument is based on the change of natural frequency of a hollow oscillator when filled with different fluids. Equation (2) can be derived considering a system represented by a hollow body of mass M_0 under vacuum and volume V (P, T) filled with a sample of density ρ (P, T). This body would be suspended on a spring with a stiffness K (P, T). The expressions for coefficients A and B are:

$$A = \frac{K}{4\pi^2 V}, \quad (3)$$

$$B = \frac{M_0}{V}. \quad (4)$$

Although A and B in equation (2) are physically meaningful parameters of the oscillating tube, they are usually evaluated by calibration with at least two fluids of known density. If the aim

of the work is to measure density as a function of temperature and pressure, one should have accurate data for the two or more calibration fluids for the entire range of T and P , since they are temperature and pressure dependent. The work of Lagourette *et al.* [20] and Sousa *et al.* [21] visualized an alternative calibration method based on the experimental determination of the vibrating period of the evacuated tube, $\tau_0(T)$, assuming that the stiffness parameter K does not depend on P . As a consequence of this assumption, $A(T, P)$ and $B(T, P)$ would vary with P in the same way and A/B would be independent of P . The resulting working equation in this case is represented by equation (5):

$$\rho = \frac{M_0}{V} \left(\frac{\tau^2}{\tau_0^2} - 1 \right) = B \left(\frac{\tau^2}{\tau_0^2} - 1 \right). \quad (5)$$

This equation would thus correspond to a one fluid calibration method, provided that $\tau_0(T)$ is known. The most difficult part of this method consists on obtaining the latter experimentally, since perfect vacuum can never be attained. Consequently, the uncertainty of the measurements would be considerably affected. In this sense, the period of four certified density calibrants, water, toluene, glycerin and tetrachloroethylene, was measured and then, through simple mathematical manipulations of the equations, it is possible to obtain suitable values of $\tau_0(T)$ in order to use equation (5). Further information on the derivation of this method can be found in references [19,21].

2.2.3. Manufacture of IoNanofluids

Based on previous work [6,7,10] and on the suggestions of Fukushima and co-workers [11,12], the IoNanofluids were prepared using a sonication probe (Sonicator Sonics & Materials, VC50) to disperse (0.5 and 1%) mass fraction of MWCTNs in all three ionic liquids. Contrary to the above-cited work [6,7], the present goal was to obtain a fluid and not a gel in order to acknowledge the possible use of these IoNanofluids as a heat transfer fluids. In that sense, these substances had to possess some fluidity and, therefore, were synthesized under different conditions. It is worth mentioning that no surfactant was added to the emulsion since any thermal conductivity values would be masked due to the presence of such substances and it was our intention to acquire the most truthful data possible. In fact, Murshed *et al.* demonstrated in a recent publication [22] that all surfactant-added nanofluids have a larger enhancement of the thermal conductivity compared to the same nanofluids without any surfactant, for nanofluids based in water. Moreover, while addition of surfactant contributes in enhancing the effective thermal conductivity, the nanoparticle clustering showed negative impact on both the stability and the effective thermal conductivity of nanofluids. The uncertainty in the IoNanofluids mass fraction was found to be $u(w) = 0.0004$.

The demonstration that aggregates are not present in the IoNanofluids can only be made by dynamical light scattering studies, a procedure used for nanofluids before. However, in the case of black nanofluids, these studies are more difficult to achieve and were not performed in the current study. However, our previous experience with other IoNanofluids, suggest that no aggregation is present at a microscopic scale, as the suspension could sediment with the presence of surfactants, which was not observed for several months.

3. Results and discussion

3.1. Thermal conductivity

3.1.1. Pure ionic liquids

The thermal conductivity of the three pure ionic liquids and several IoNanofluids was measured at temperatures between

(293 and 343) K at 0.1 MPa. In the case of the pure ionic liquids, the water content was confirmed using Coulometric Karl Fischer titration after the thermal conductivity (and density) measurements, values that are presented in table 3. Some increase in the water content was to be expected but, particularly in the case of the thermal conductivity, the increase was minor.

Table 4 displays the values obtained for the pure ionic liquids, which generally tend to softly decrease with temperature. The exception to this tendency is the thermal conductivity of [C₂mim][dca] at $T = 323$ K, where a considerable oscillation can be observed. Such a fact can be attributed to the sensitivity of the KD2 Pro to the variation of viscosity of the fluid being measured [10,23], given that the viscosity of ionic liquids decreases with the increase of temperature.

The results obtained for each liquid were fitted to a straight line, according to equation (6), and table 5 shows the coefficients obtained, as well as the root mean square deviations of the fits.

$$\lambda(W \cdot m^{-1} \cdot K^{-1}) = \alpha_1 + \alpha_2(T/K). \quad (6)$$

Figure 1 shows the variation of the thermal conductivity of the pure ionic liquids with temperature, for the range between (293 and 343) K at 0.1 MPa. It can be seen that the variation is linear for all three ionic liquids. For [C₂mim][dca] no data point departs from linearity by more than $\pm 1.06\%$ (except for the value at $T = 323$ K, which undoubtedly differs from the rest of the data). The root mean square deviation of the fits did not exceed $3.83 \text{ mW} \cdot m^{-1} \cdot K^{-1}$, about 2%. For [C₄mim][dca], no data point departs from linearity by more than $\pm 1.4\%$ (except for the value at $T = 323$ K, which departs from linearity by +2.5%). The root mean square deviation of the fits did not exceed $2.73 \text{ mW} \cdot m^{-1} \cdot K^{-1}$, about 1.6%. Finally, for [C₄mpyr][dca], no data point departs from linearity by more than $\pm 1.3\%$. The root mean square deviation of the fits did not exceed $1.74 \text{ mW} \cdot m^{-1} \cdot K^{-1}$, about 1.1%. For all three pure ionic liquids, the variation of the values is almost independent with the variation of temperature.

The uncertainties of the experimental data were estimated to obtain the expanded uncertainty, U_G , using the normal procedure. This parameter is obtained multiplying the combined standard uncertainty, u_G , by an expansion factor, k , that depends of the confidence limit of the interval, usually 95%, and therefore $k = 2$. The expression to calculate the standard uncertainty is the following:

$$U_G^2 = u_{\text{cal}}^2 + u_{\text{exp}}^2, \quad (7)$$

where u_{cal} represents the uncertainty of the calibration (the standard deviation of the calibration constant, 0.034) and u_{exp} the uncertainty of the each experimental measurement, (the standard deviation of the average thermal conductivity at each temperature, taken from 8 to 10 measurements). The value of U_G is therefore given by:

$$U_G = k \times u_G. \quad (8)$$

The major contribution for the uncertainty results from the uncertainty of each experimental measurement. The uncertainty obtained fluctuated between $(0.012 \text{ and } 0.021) \text{ W} \cdot m^{-1} \cdot K^{-1}$ (6.7

TABLE 4

Thermal conductivities of pure ionic liquids as a function of temperature, at $p = 0.1 \text{ MPa}$.^a

Ionic liquid	T/K	$\lambda/W \cdot m^{-1} \cdot K^{-1}$
[C ₂ mim][dca]	293.4	0.183 ± 0.01
	303.3	0.179 ± 0.01
	313.1	0.178 ± 0.02
	323.0	0.181 ± 0.02
	333.2	0.170 ± 0.02
	343.4	0.165 ± 0.02
[C ₄ mim][dca]	293.6	0.167 ± 0.01
	303.3	0.166 ± 0.01
	313.4	0.163 ± 0.01
	323.5	0.163 ± 0.01
	333.7	0.153 ± 0.01
	344.2	0.150 ± 0.01
[C ₄ mpyr][dca]	293.5	0.155 ± 0.01
	303.2	0.155 ± 0.01
	313.3	0.153 ± 0.01
	323.3	0.151 ± 0.01
	333.2	0.147 ± 0.01
	343.4	0.142 ± 0.02

^a Standard uncertainties are $u(T) = 0.1 \text{ K}$, $u(p) = 1 \text{ kPa}$ and the experimental expanded uncertainty, $U_G = U_G(\lambda) = 0.01 \text{ to } 0.02 \text{ W} \cdot m^{-1} \cdot K^{-1}$, with 0.95 level of confidence ($k = 2$).

to 12.5%) for [C₂mim][dca], between $(0.010 \text{ and } 0.014) \text{ W} \cdot m^{-1} \cdot K^{-1}$ (6.6 to 9.2%) for [C₄mim][dca] and between $(0.010 \text{ and } 0.017) \text{ W} \cdot m^{-1} \cdot K^{-1}$ (6.6 to 11.8%) for [C₄mpyr][dca]. The poorest case is represented by [C₂mim][dca], which exhibits only two values of thermal conductivity below 10% uncertainty. The low viscosity and the continued decrease of the latter with the increase of temperature of these ionic liquids had a greater influence on the results that would be desired. In this particular case, more than 10 measurements were acquired in order to minimize the fluctuation of the value obtained, specifically at the temperatures where this oscillation was observed. However, the results kept on fluctuating in the same fashion. In previously measured pure ionic liquids, the uncertainty of the thermal conductivity fluctuated between (6 and 7)% at a 95% confidence level, greatly influenced by the value of the calibration.

Fröba *et al.* [24] measured the thermal conductivity of [C₂mim][dca] with a stationary guarded parallel-plate instrument, with an estimated expanded uncertainty of 3%. However, these values deviate from our values between (10 and 15)%, as the temperature increases (smaller temperature slope), a value greater than the mutual uncertainty of the data. The same type of deviation occurs for [C₂mim][EtSO₄] [7], but the comparison for [C₂mim][(CF₃SO₂)₂N] and [C₆mim][(CF₃SO₂)₂N] show deviations smaller than 2%, an excellent result. No explanation was found for these discrepancies, depending on the ionic liquid studies, and the fact needs further investigation.

3.1.2. IoNanofluids

The thermal conductivities of the IoNanofluids based on [C₂mim][dca], [C₄mim][dca] and [C₄mpyr][dca], with (0.5 and 1)% mass fraction were measured at temperatures between (293 and 343) K at 0.1 MPa. Tables 6–8 show the results obtained as well as the percentage of enhancement of the thermal conductivity. This enhancement is estimated based on the thermal conductivity at the correspondent temperature of the base fluid for each case. Figures 2–4 show a plot of the thermal conductivity of the IoNanofluids as a function of temperature, for the same temperature range than the pure fluids. These figures also display the thermal conductivity of the base ionic liquid. The uncertainty of the values of thermal conductivity of the IoNanofluids fluctuated between (6.6 and 6.7)%. The situation of these suspensions is clearly

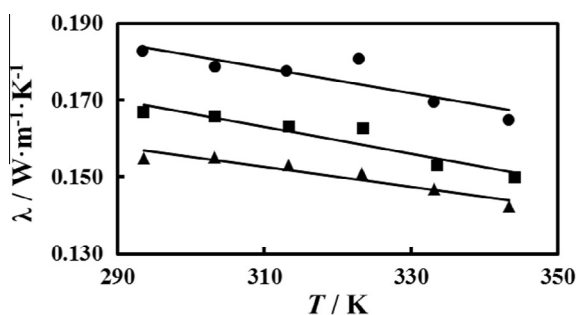
TABLE 3

Water content of the pure ionic liquids (Karl–Fischer coulometer).

Ionic liquid	[C ₂ mim][dca]	[C ₄ mim][dca]	[C ₄ mpyr][dca]
After drying H ₂ O/10 ^{−6}	234.7 ± 48.6	324.9 ± 86.4	349.6 ± 47.9
After measuring λ H ₂ O/10 ^{−6}	488.9 ± 58.6	683.6 ± 41.7	637.0 ± 57.0
After measuring ρ H ₂ O/10 ^{−6}	1007.4 ± 55.4	741.2 ± 20.3	1601.3 ± 84.5

TABLE 5Coefficients of equation (6) for pure ionic liquids and IoNanofluids.^a

Substance	$a_1 \pm s_{a1}$ /W · m ⁻¹ · K ⁻¹	$10^5 (a_2 \pm s_{a2})$ /W · m ⁻¹ · K ⁻²	$10^5 s$ /W · m ⁻¹ · K ⁻¹
[C ₂ mim][dca]	0.28027 ± 0.029	-32.873 ± 9.2	383
[C ₄ mim][dca]	0.27205 ± 0.021	-35.136 ± 6.5	273
[C ₄ mpyr][dca]	0.23328 ± 0.013	-25.989 ± 4.2	174
[C ₂ mim][dca] 0.5% w/w MWCNTs	0.22242 ± 0.0055	-12.753 ± 1.7	65
[C ₂ mim][dca] 1% w/w MWCNTs	0.23141 ± 0.0041	-13.128 ± 1.3	50
[C ₄ mim][dca] 0.5% w/w MWCNTs	0.20176 ± 0.00038	-9.959 ± 0.12	4.5
[C ₄ mim][dca] 1% w/w MWCNTs	0.21211 ± 0.0047	-11.124 ± 1.5	56
[C ₄ mpyr][dca] 0.5% w/w MWCNTs	0.18059 ± 0.00065	-6.760 ± 0.20	7.9
[C ₄ mpyr][dca] 1% w/w MWCNTs	0.21204 ± 0.0082	-14.775 ± 2.6	98

^a With expanded uncertainty at 0.95 level of confidence ($k = 2$).**FIGURE 1.** Plot of thermal conductivity of pure ionic liquids as a function of temperature. ● – [C₂mim][dca]; ■ – [C₄mim][dca]; ▲ – [C₄mpyr][dca]. Lines are given by equation (10) with coefficients shown in table 10.

different than the one stated for the pure ionic liquids because the viscosity is considerably greater due to the addition of MWCNTs. As expected, the dispersion of data obtained at each temperature was almost negligible and the uncertainty values are almost entirely dictated by the calibration.

The increase in the thermal conductivity of the base ionic liquid is easily observed, as is the stabilization of the thermal property, i.e., the decrease in thermal conductivity as a function of temperature is smaller due to the addition of MWCNTs. From an application perspective, such feature could be significant if the process in question would require a heat transfer fluid that can be used in a range of temperature without compromising its efficiency. Additionally, and as expected, the enhancement of the thermal conductivity is directly proportional to the mass fraction of the nanomaterial. The fact that the enhancement can go up to 16.5% with a 1% mass fraction of MWCNTs and its dependence of temperature in the studied range supports the prospect of using these suspensions as heat transfer fluids.

TABLE 6Thermal conductivities of IoNanofluids based on [C₂mim][dca] as a function of temperature, at $p = 0.1$ MPa.^a

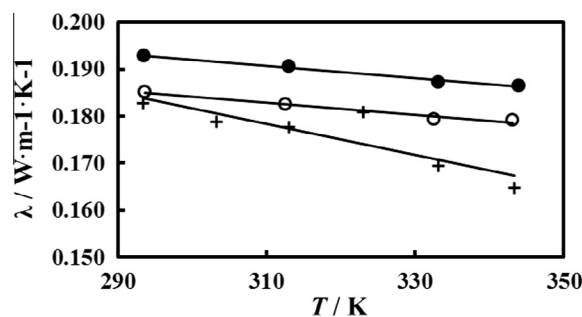
Substance	T/K	$\lambda/W \cdot m^{-1} \cdot K^{-1}$	Enhancement/%
[C ₂ mim][dca] 0.5% w/w MWCNTs	293.6	0.185	1.33
	312.6	0.183	2.74
	332.5	0.179	5.82
	343.1	0.179	8.82
[C ₂ mim][dca] 1% w/w MWCNTs	293.5	0.193	5.49
	313.1	0.191	7.35
	333.2	0.187	10.42
	343.9	0.187	13.25

^a Standard uncertainties are $u(T) = 0.1$ K, $u(p) = 1$ kPa and the experimental expanded uncertainty, $U_c = U_c(\lambda) = 0.01$ W · m⁻¹ · K⁻¹, with 0.95 level of confidence ($k = 2$).**TABLE 7**Thermal conductivities of IoNanofluids based on [C₄mim][dca] as a function of temperature, at $p = 0.1$ MPa.^a

Substance	T/K	$\lambda/W \cdot m^{-1} \cdot K^{-1}$	Enhancement/%
[C ₄ mim][dca] 0.5% w/w MWCNTs	293.7	0.173	3.51
	313.0	0.171	4.60
	333.3	0.169	10.37
	343.3	0.168	11.95
[C ₄ mim][dca] 1% w/w MWCNTs	293.7	0.180	7.72
	312.8	0.177	8.79
	332.8	0.175	14.19
	343.5	0.174	16.51

^a Standard uncertainties are $u(T) = 0.1$ K, $u(p) = 1$ kPa, $u(w) = 0.0004$ and the experimental expanded uncertainty, $U_c = U_c(\lambda) = 0.01$ W · m⁻¹ · K⁻¹, with 0.95 level of confidence ($k = 2$).**TABLE 8**Thermal conductivities of IoNanofluids based on [C₄mpyr][dca] as a function of temperature, at $p = 0.1$ MPa.^a

Substance	T/K	$\lambda/W \cdot m^{-1} \cdot K^{-1}$	Enhancement/%
[C ₄ mpyr][dca] 0.5% w/w MWCNTs	293.1	0.161	3.71
	312.4	0.160	4.20
	333.4	0.158	7.70
	343.7	0.157	10.55
[C ₄ mpyr][dca] 1% w/w MWCNTs	293.7	0.168	8.68
	312.6	0.167	8.78
	333.0	0.162	10.23
	343.7	0.162	13.70

^a Standard uncertainties are $u(T) = 0.1$ K, $u(p) = 1$ kPa, $u(w) = 0.0004$ and the experimental expanded uncertainty, $U_c = U_c(\lambda) = 0.01$ W · m⁻¹ · K⁻¹, with 0.95 level of confidence ($k = 2$).**FIGURE 2.** Plot of thermal conductivity of pure [C₂mim][dca] and its IoNanofluids as a function of temperature. ● – [C₂mim][dca] pure; ○ – INF 0.5% w/w MWCNTs; + – INF 1% w/w MWCNTs. Lines are given by equation (10) with coefficients shown in table 10.

Figures 5 and 6 show the plot of the enhancement, $(\lambda_{INF}/\lambda_{IL} - 1)$, where λ_{INF} is the thermal conductivity of the IoNanofluid and λ_{IL} the thermal conductivity of the base ionic liquid, as a function of

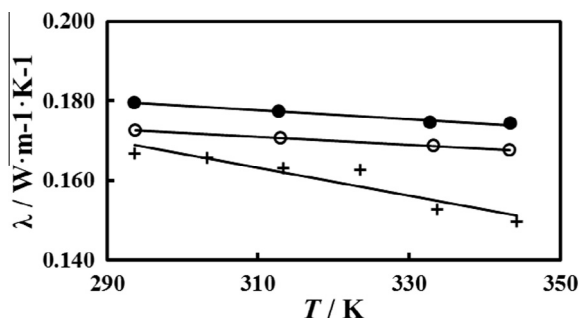


FIGURE 3. Plot of thermal conductivity of pure $[C_4mim][dca]$ and its IoNanofluids as a function of temperature. ● – $[C_4mim][dca]$ pure; ○ – INF 0.5% w/w MWCNTs; + – INF 1% w/w MWCNTs. Lines are given by equation (10) with coefficients shown in table 10.

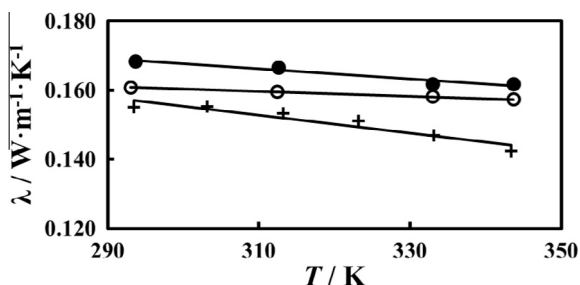


FIGURE 4. Plot of thermal conductivity of pure $[C_4mpyr][dca]$ and its IoNanofluids as a function of temperature. ● – $[C_4mpyr][dca]$ pure; ○ – INF 0.5% w/w MWCNTs; + – INF 1% w/w MWCNTs. Lines are given by equation (10) with coefficients shown in table 10.

temperature, and volume fraction, respectively. The work of Fukushima *et al.* [12,13] suggested an increase in the organization of the fluid when carbon nanotubes are added to it. Though it is not entirely clear at this time what organized structure exists in these suspensions, such fact is in agreement with an increase in thermal conductivity since it is well known that solids conduct heat much more effectively than liquids. Based on this idea, when comparing the results between different base ionic liquids, it is possible to state that $[C_4mim][dca]$ is the one that benefits more from the addition of MWCNTs.

The enhancement of the thermal conductivity of this ionic liquid is higher in either mass fraction in the majority of the temperature values studied, which could support the idea of a greater increase in the organization of the liquid nanostructure, favouring a higher transfer of heat. Since the anion is the same for all three ionic liquids and if we take into account the idea of the increase

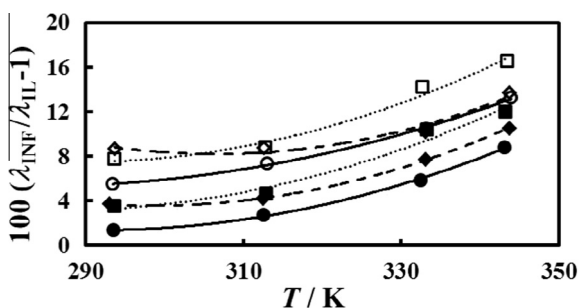


FIGURE 5. Plot of thermal conductivity enhancement of INFs as a function of temperature. Full symbols – INF 0.5% w/w MWCNTs; open symbols – IL 1% w/w MWCNTs. —, ●, ○ – $[C_2mim][dca]$; —, ■, □ – $[C_4mim][dca]$; —, —, ◆, ◇ – $[C_4mpyr][dca]$.

of organization when adding MWCNTs, we could infer that the cation is the controlling factor for the differences in structure of the pure ionic liquids, and also for the IoNanofluids.

The compounds studied can be separated into head group (imidazolium or pyrrolidinium with methyl substitution), an aliphatic side chain and an anion (the same). The data obtained justifies that by changing the side chain length, the enhancement in the thermal conductivity increases, possibly due to a better interaction between this chain and the carbon nanotube surface (non-polar entities) that facilitates heat transfer. The same effect was found for the $[C_nmim][(CF_3SO_2)_2N]$ family [7], ranging from $n = 2$ to $n = 8$.

The change of the head group does not seem to affect the enhancement, except for volume fraction of the nanotube greater than 0.04, where the methylimidazolium seems to win.

Finally, we can compare data for liquids that have the same cation, $[C_2mim]$, and different anions, $[N(CN)_2]$, $[C_2H_5OSO_3]$ [10] and $[(CF_3SO_2)_2N]$ [7]. The anion structure affects the enhancement, with the $[(CF_3SO_2)_2N]$ salt having the smallest and the $[C_2H_5OSO_3]$ the highest. The same result is obtained when we compare the liquids based on the $[C_4mim]$ cation, with the $[(CF_3SO_2)_2N]$ salt having smaller enhancement than the $[N(CN)_2]$ one.

Depending on the ionic liquid and the quantity of MWCNTs, the variation of the thermal conductivity can be seemingly linear or described by a power function. Such dissimilarity increases the difficulty of establishing a model that allows the accurate prediction of the enhancement of the thermal conductivity of this sort of suspensions. Recent experimental results attested that one of the models conceived for suspensions of cylindrical particles in ionic liquids display a great lack of agreement between experience and theory [10]. For the systems studied here the results obtained are displayed in figure 7, where the thermal conductivity enhancement at $T = 293$ K and 0.1 MPa is plotted as a function of the volume fraction of the carbon nanotubes in the IoNanofluid. It is very clear that the theoretical values are much less than the experimental ones, that the theory is not sensitive to the base ionic liquid and that the volume fraction dependence is weaker.

One of the variables of this model that significantly influences the outcome is the thermal conductivity of the ionic liquid–MWCNTs interface, to which no specific values exist to date. Consequently, further understanding on the interactions that take place at this interface is required in order to envisage an accurate model for the prediction of the abovementioned effect [7,10]. Studies using molecular simulation are under way to study structure and dynamics of ionic liquids in contact with carbon nanomaterials, such as graphene sheets and nanotubes, and results will be presented soon [25].

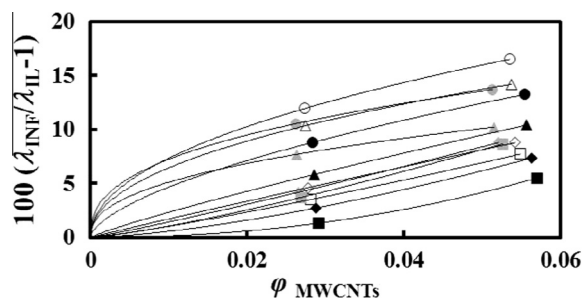


FIGURE 6. Plot of thermal conductivity enhancement of the IoNanofluids as a function of the volume fraction of MWCNTs. ■, □, ■ – $T = 293$ K; ◆, ◇, ◆ – $T = 313$ K; ▲, △, ▲ – $T = 333$ K; ●, ○, ● – $T = 343$ K; full symbols: – IoNanofluids based on $[C_2mim][dca]$; empty symbols: – ionanofluids based on $[C_4mim][dca]$; grey symbols: – ionanofluids based on $[C_4mpyr][dca]$. Lines are just drawn for clarity, having no special meaning.

3.2. Density

As mentioned above, the method used to calibrate the densimeter relies on the contribution of the parameter τ_0 . According to reference [19], by applying equation (5) to two calibrating fluids, whose density values $\rho_{1,\text{ref}}$ and $\rho_{2,\text{ref}}$ are accurately known as a function of temperature and pressure, and dividing the two equations in order to eliminate the B parameter, we obtain a new equation having τ_0 as a single unknown variable. Solving this last equation for τ_0 we obtain equation (9):

$$\tau_{0,\text{calc}} = \left(\frac{\rho_{1,\text{ref}}\tau_2^2 - \rho_{2,\text{ref}}\tau_1^2}{\rho_{1,\text{ref}} - \rho_{2,\text{ref}}} \right)^{1/2}, \quad (9)$$

where τ_1 and τ_2 are experimentally obtained vibrating periods for the respective reference liquids at each fixed temperature. The set of calibrants aforementioned cover the range of densities of interest and, following the procedure on reference [19], we obtain an associated standard uncertainty of $u(\rho) = 0.22 \text{ kg} \cdot \text{m}^{-3}$ for both pure ionic liquids and IoNanofluids.

3.2.1. Pure Ionic Liquids

The density of the three pure ionic liquids and several IoNanofluids was measured at temperatures between (293 and 343) K at 0.1 MPa. The results for the pure liquids can be found in table 9, which shows a steady decrease on the value of the property as a function of temperature. The results obtained for each liquid were fitted to a function, according to equation (10), and table 10 shows the coefficients obtained, as well as the root mean square deviations of the fits.

$$\rho(\text{kg} \cdot \text{m}^{-3}) = a_1 + a_2 T(\text{K}) + a_3 T^2(\text{K}). \quad (10)$$

It was first attempted to fit the results to a straight line but fitting the latter equation provided significantly lower values of standard error. From the table, it can be acknowledged that the root mean square deviation of the fits did not exceed $0.285 \text{ kg} \cdot \text{m}^{-3}$ for any of the fluids in question. Also, no data departs from the fit by more than $\pm 0.05\%$ for the pure ionic liquids and $\pm 0.03\%$ for the suspensions.

Contrary to the case of the thermal conductivity, there are numerous data of ionic liquid densities to which is possible to compare our results with. Figure 8 shows the existing data for the density of $[\text{C}_2\text{mim}][\text{dca}]$, compared with the present results. The comparison shows that there are two distinctive trends, which do not agree within their mutual uncertainty, apart from a very different value (single point) obtained by Yoshida *et al.* [26], well apart from the others ($\sim 2.1\%$). The upper results were obtained

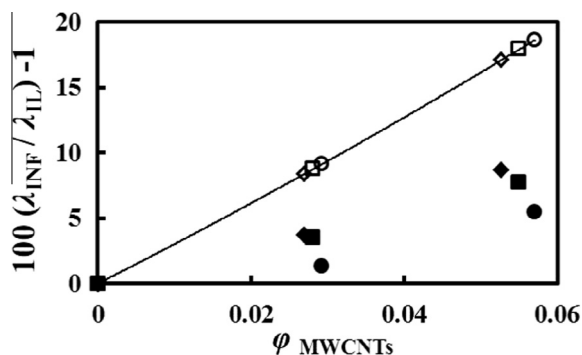


FIGURE 7. Plot of thermal conductivity enhancement of the IoNanofluids, as a function of the volumetric fraction of MWCNTs, at $T = 293 \text{ K}$ and 0.1 MPa . Open symbols, experiment. Closed symbols theory. \bullet , \circ – $[\text{C}_2\text{mim}][\text{dca}]$; \blacksquare , \square – $[\text{C}_4\text{mim}][\text{dca}]$; \blacklozenge , \diamond – $[\text{C}_4\text{mpyr}][\text{dca}]$.

TABLE 9

Densities of the pure ionic liquids as a function of temperature, at $p = 0.1 \text{ MPa}$.^a

T/K	$\rho/\text{kg} \cdot \text{m}^{-3}$		
	$[\text{C}_2\text{mim}][\text{dca}]$	$[\text{C}_4\text{mim}][\text{dca}]$	$[\text{C}_4\text{mpyr}][\text{dca}]$
293.2	1107.5	1064.5	1018.3
303.2	1100.4	1057.5	1011.8
313.2	1093.5	1051.0	1006.1
323.2	1087.0	1045.1	1000.6
333.2	1081.0	1040.6	995.6
343.2	1076.1	1035.7	991.3

^a Standard uncertainties are $u(T) = 0.1 \text{ K}$, $u(p) = 1 \text{ kPa}$ and the experimental expanded uncertainty, $U_c = U_c(\rho) = 0.2 \text{ kg} \cdot \text{m}^{-3}$, with 0.95 level of confidence ($k = 2$).

by Fröba *et al.* [27], Wong *et al.* [28], Soriano *et al.* [29] and Klomfar *et al.* [30], while the lower end results show the values obtained by Schreiner *et al.* [31], Freire *et al.* [16] and Quijada-Maldonado *et al.* [32]. Both sets of results differ by more than 0.7%. This result is more expressed in the insertion, where the deviations from equation (10) are displayed as a function of temperature. Our results agree with the lower data set, within $\pm 0.2\%$, or within the mutual uncertainty of the data. In order to check the results in our laboratory, different measurements were performed by Molias *et al.* [33], with a smaller uncertainty (DSA 5000 M, 0.05%). These results confirm the lower rim tendency of the data, agreeing with the present data within their mutual uncertainty.

With respect to $[\text{C}_4\text{mim}][\text{dca}]$, the results nearest to ours are the ones of Seoane *et al.* [15], while the remainders [34,35] deviate from the ones obtained in the present work around (-0.2 to 0.4%), especially at the higher temperatures. Our previously reported data [36], measured with a different densimeter, agrees with the present one within 0.05% up to $T = 323.15 \text{ K}$ and -0.25% at 243.15 K . For $[\text{C}_4\text{mpyr}][\text{dca}]$, there are three sets of data. One published by Sanchez *et al.* [34], which differ approximately 9% from our data for each temperature. Results presented by Blahut and Dohna [37] agree with our data to within -0.2% . Recently, González and Corderí [38] presented one single point, at $T = 298.15 \text{ K}$, that deviates from our correlated data by -0.15% .

The difference between the data herein presented and other published sets of data by more than their mutual uncertainty (0.2 to 0.5)% might be due to dissimilarities in the techniques used to handle and/or to dry the ionic liquids or to the purity of samples.

3.2.2. IoNanofluids

The densities of the IoNanofluids based on $[\text{C}_2\text{mim}][\text{dca}]$, $[\text{C}_4\text{mim}][\text{dca}]$ and $[\text{C}_4\text{mpyr}][\text{dca}]$, with (0.5 and 1)% mass fraction were measured at temperatures between (293 and 343) K at 0.1 MPa. Tables 11–13 show the results obtained as well as the percentage of enhancement of the density. As expected, the enhancement is very small due to extremely high difference in densities between the ionic liquids and the MWCNTs, reaching its peak at 0.65% for the case of the IoNanofluid $[\text{C}_4\text{mim}][\text{dca}]$ 1% w/w at $T = 313 \text{ K}$. Again, from an application standpoint as heat transfer fluids, such low change in the density values by the addition of the MWCNTs can represent a positive outcome. Considering the four thermophysical properties of a heat transfer fluid necessary to design a heat transfer unit (thermal conductivity, heat capacity, viscosity and density), an increase in density represents a decrease in the principal design parameter, the heat transfer area, which in turn leads to a decrease in capital and operational costs [5]. Therefore, a proper balance between these properties must be accomplished. Although a greater increase in the density would be preferable, this very low variation in density by the addition of MWCNTs indicates that there is one property less that can

TABLE 10

Coefficients of equation (10) for pure ionic liquids and IoNanofluids.^a

Fluid	$a_1 \pm s_{a1}/\text{kg} \cdot \text{m}^{-3}$	$(a_2 \pm s_{a2})/\text{kg} \cdot \text{K}^{-1} \cdot \text{m}^{-3}$	$10^5 (a_3 \pm s_{a3})/\text{kg} \cdot \text{K}^{-2} \cdot \text{m}^{-3}$	$s/\text{kg} \cdot \text{m}^{-3}$
[C ₂ mim][dca]	1555.81 ± 34	−2.294 ± 0.20	260.892 ± 33	0.204
[C ₄ mim][dca]	1564.43 ± 47	−2.672 ± 0.30	329.757 ± 47	0.285
[C ₄ mpyr][dca]	1423.55 ± 11	−2.102 ± 0.072	245.525 ± 11	0.069
[C ₂ mim][dca] 0.5% w/w MWCNTs	1588.89 ± 2.1	−2.472 ± 0.013	287.159 ± 2.0	0.012
[C ₂ mim][dca] 1% w/w MWCNTs	1556.03 ± 39	−2.258 ± 0.25	254.011 ± 39	0.236
[C ₄ mim][dca] 0.5% w/w MWCNTs	1496.25 ± 14	−2.189 ± 0.086	248.680 ± 14	0.083
[C ₄ mim][dca] 1% w/w MWCNTs	1331.62 ± 42	−1.113 ± 0.27	75.948 ± 42	0.255
[C ₄ mpyr][dca] 0.5% w/w MWCNTs	1428.40 ± 19	−2.117 ± 0.12	247.461 ± 19	0.113
[C ₄ mpyr][dca] 1% w/w MWCNTs	1400.33 ± 34	−1.927 ± 0.21	219.137 ± 33	0.204

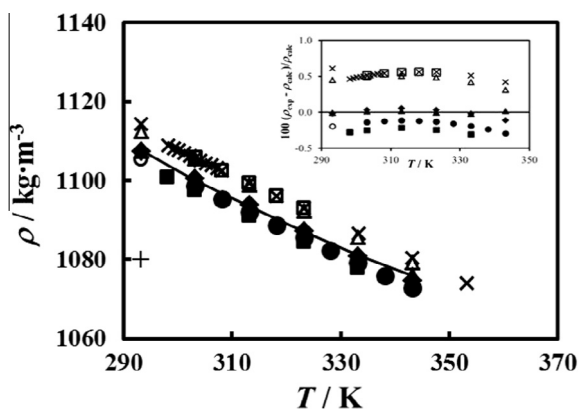
^a With expanded uncertainty at 0.95 level of confidence ($k = 2$).

FIGURE 8. Plot of density of [C₂mim][dca] as a function of temperature. + Yoshida et al. [25]; Δ Froba et al. [26]; □ Wong et al. [27]; × Soriano et al. [28]; ■ Schreiner et al. [29]; ● Quijada-Maldonado et al. [30]; ○ Nieto de Castro et al. [31]; ▲ present work. In the insert the relative deviations (%) between the density measurements obtained in this work (ρ_{exp}), and those reported in literature (ρ_{lit}) as function of temperature, using equation (10) as the reference.

influence the heat transfer area and the mentioned balance will be more dependent on the variation of the remainder properties.

Figures 9–11 contain a plot of the density of the IoNanofluids as a function of temperature, including the densities of the corresponding base ionic liquid presented in the previous section in

order to allow a better visual perception of the enhancement due to the addition of MWCNTs. The small increase on the density of the base ionic liquid is easily observed, as the values are very close between them for each temperature. As it was stated for the thermal conductivity, the enhancement of the density is directly proportional to the mass fraction of the nanomaterial.

TABLE 12

Densities of Ionanofluids based on [C₄mim][dca] as a function of temperature, at $p = 0.1 \text{ MPa}$.^a

Substance	T/K	$\rho/\text{kg} \cdot \text{m}^{-3}$	Enhancement/%
[C ₄ mim][dca] 0.5% w/w MWCNTs	293.2	1068.1	0.34
	303.2	1061.1	0.35
	313.2	1054.4	0.32
	323.2	1048.5	0.32
	333.2	1042.9	0.22
	343.2	1037.8	0.20
[C ₄ mim][dca] 1% w/w MWCNTs	293.2	1070.5	0.56
	303.2	1063.9	0.61
	313.2	1057.8	0.65
	323.2	1050.9	0.56
	333.2	1045.0	0.42
	343.2	1039.1	0.33

^a Standard uncertainties are $u(T) = 0.1 \text{ K}$, $u(p) = 1 \text{ kPa}$, $u(w) = 0.0004$ and the experimental expanded uncertainty, $U_c = U_c(\rho) = 0.2 \text{ kg} \cdot \text{m}^{-3}$, with 0.95 level of confidence ($k = 2$).

TABLE 11

Densities of IoNanofluids based on [C₂mim][dca] as a function of temperature, at $p = 0.1 \text{ MPa}$.^a

Substance	T/K	$\rho/\text{kg} \cdot \text{m}^{-3}$	Enhancement/%
[C ₂ mim][dca] 0.5% w/w MWCNTs	293.2	1110.9	0.30
	303.2	1103.3	0.27
	313.2	1096.3	0.25
	323.2	1089.8	0.26
	333.2	1083.9	0.27
	343.2	1078.6	0.24
[C ₂ mim][dca] 1% w/w MWCNTs	293.2	1112.4	0.44
	303.2	1104.8	0.41
	313.2	1098.4	0.44
	323.2	1091.5	0.42
	333.2	1085.6	0.43
	343.2	1080.4	0.40

^a Standard uncertainties are $u(T) = 0.1 \text{ K}$, $u(p) = 1 \text{ kPa}$, $u(w) = 0.0004$ and the experimental expanded uncertainty, $U_c = U_c(\rho) = 0.2 \text{ kg} \cdot \text{m}^{-3}$, with 0.95 level of confidence ($k = 2$).

TABLE 13

Densities of Ionanofluids based on [C₄mpyr][dca] as a function of temperature, at $p = 0.1 \text{ MPa}$.^a

Substance	T/K	$\rho/\text{kg} \cdot \text{m}^{-3}$	Enhancement/%
[C ₄ mpyr][dca] 0.5% w/w MWCNTs	293.2	1020.6	0.22
	303.2	1014.2	0.23
	313.2	1008.4	0.23
	323.2	1002.9	0.23
	333.2	997.8	0.22
	343.2	993.6	0.23
[C ₄ mpyr][dca] 1% w/w MWCNTs	293.2	1023.9	0.55
	303.2	1017.5	0.56
	313.2	1012.1	0.60
	323.2	1006.6	0.60
	333.2	1001.5	0.59
	343.2	997.3	0.61

^a Standard uncertainties are $u(T) = 0.1 \text{ K}$, $u(p) = 1 \text{ kPa}$, $u(w) = 0.0004$ and the experimental expanded uncertainty, $U_c = U_c(\rho) = 0.2 \text{ kg} \cdot \text{m}^{-3}$, with 0.95 level of confidence ($k = 2$).

Shown in figure 12 is the plot of the enhancement as a function of volume fraction, in a similar way that was presented for the thermal conductivity. Once again, it is illustrated that the variation of a property can depend on the ionic liquid, quantity of nanomaterial and temperature. Such dependence complicates the determination of a model that can predict the enhancement of the density of an ionic liquid with suspended nanoparticles. While the range of enhancement for density is low, rigorous and reliable data are needed in order to plan the use of these substances in applications.

As done with thermal conductivity data in previous work [10], we propose a comparison between experimental data and calculated values of densities using a model. In order to calculate the value of the density of the liquids with suspended particles, the work of Pak and Cho [39] was modified by Ribeiro [40] to obtain equation (11):

$$\rho = (1 - \varphi_p)\rho_{IL} + \varphi_p\rho_p, \quad (11)$$

where ρ_{IL} and ρ_p are the densities of the ionic liquid and particles, respectively, and φ_p represents the volume fraction of the suspended particles. Figure 13 shows a plot of the density as a function of the volume fraction of MWCNTs for the experimental data and the calculated data using equation (11). Density of the MWCNTs used was taken from table 2 (average value of $185 \text{ g} \cdot \text{cm}^{-3}$). Although it may seem that the data are considerably apart and the slope is noticeably different, the experimental values do not differ by more than $(-2.43 \text{ for } 0.5\%)$ w/w mass fraction IoNanofluids and -4.74% for the 1% w/w mass fraction IoNanofluids. Such a divergence may be due to the fact that the equation fails to take in to account for, as an example, specific interaction forces between the two kinds of material. As it was said for the case of thermal conductivity, further understanding on the interactions that take place at the solid-liquid interface is required.

Regarding structural interpretations, it can be seen that the liquid that has the highest density is $[\text{C}_2\text{mim}][\text{dca}]$, and the lowest density is $[\text{C}_4\text{mpyr}][\text{dca}]$, probably because the increase in the alkyl side chain makes the structure of the liquid less packed, and that planar head groups pack much better than non-planar. In the IoNanofluids the enhancement is so small that no discernible difference in the enhancements is found, the packaging trend being similar to the pure ionic liquids. This fact can have two possible interpretations. Either the ions enter the carbon nanotubes (2 to 6) nm diameter, as shown in the molecular simulation studies

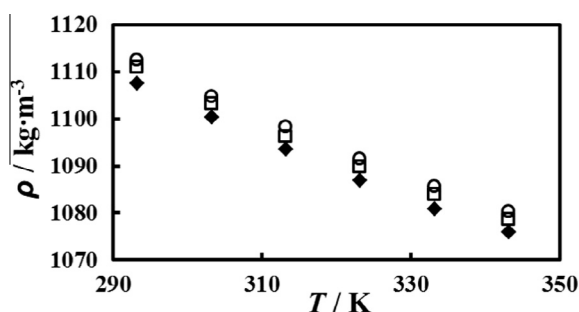


FIGURE 9. Plot of density of IoNanofluids based on $[\text{C}_2\text{mim}][\text{dca}]$ and of the pure ionic liquid as a function of temperature. \blacklozenge – $[\text{C}_2\text{mim}][\text{dca}]$ pure; \square – $[\text{C}_2\text{mim}][\text{dca}]$ INF 0.5% w/w MWCNTs; \circ – $[\text{C}_2\text{mim}][\text{dca}]$ INF 1% w/w MWCNTs.

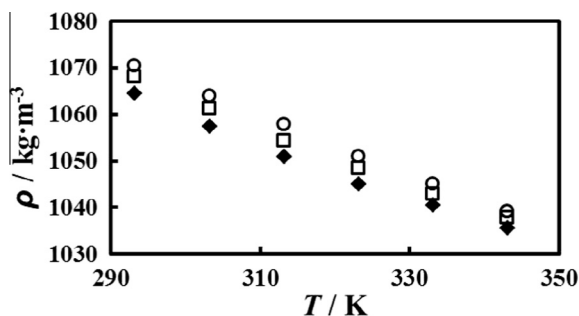


FIGURE 10. Plot of density of IoNanofluids based on $[\text{C}_4\text{mim}][\text{dca}]$ and of the pure ionic liquid as a function of temperature. \blacklozenge – $[\text{C}_4\text{mim}][\text{dca}]$ pure; \square – $[\text{C}_4\text{mim}][\text{dca}]$ 0.5% w/w MWCNTs; \circ – $[\text{C}_4\text{mim}][\text{dca}]$ 1% w/w MWCNTs.

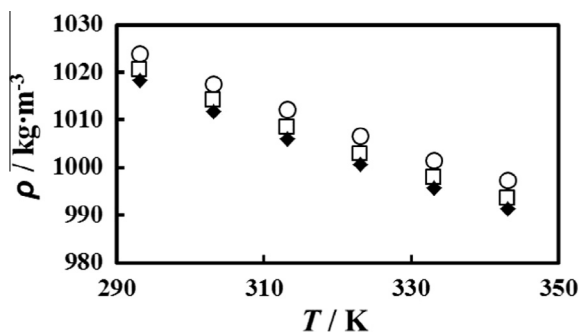


FIGURE 11. Plot of density of IoNanofluids based on $[\text{C}_4\text{mpyr}][\text{dca}]$ and of the pure ionic liquid as a function of temperature. \blacklozenge – $[\text{C}_4\text{mpyr}][\text{dca}]$ pure; \square – $[\text{C}_4\text{mpyr}][\text{dca}]$ 0.5% w/w MWCNTs; \circ – $[\text{C}_4\text{mpyr}][\text{dca}]$ 1% w/w MWCNTs.

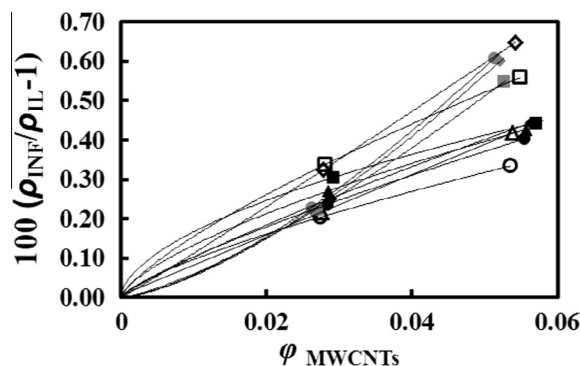


FIGURE 12. Plot of density enhancement of the IoNanofluids as a function of the volume fraction of MWCNTs. $\blacksquare, \square, \blacklozenge, \lozenge, \blacktriangle, \triangle, \bullet, \circ, \bullet, \circ$ – $T = 293 \text{ K}; \blacklozenge, \lozenge, \blacktriangle, \triangle, \bullet, \circ, \bullet, \circ$ – $T = 313 \text{ K}; \blacktriangle, \triangle, \bullet, \circ, \bullet, \circ$ – $T = 333 \text{ K}; \bullet, \circ, \bullet, \circ$ – $T = 343 \text{ K}$; Full symbols: – IoNanofluids based on $[\text{C}_2\text{mim}][\text{dca}]$; empty symbols: – IoNanofluids based on $[\text{C}_4\text{mim}][\text{dca}]$; grey symbols: – IoNanofluids based on $[\text{C}_4\text{mpyr}][\text{dca}]$.

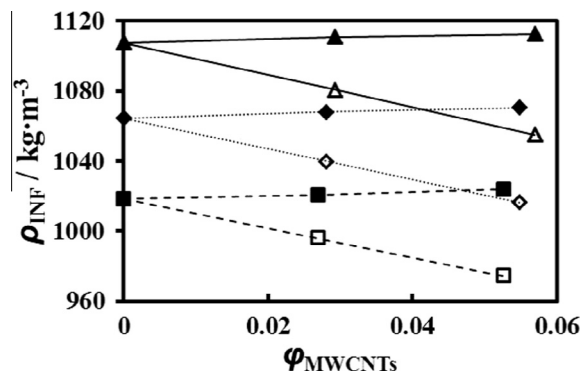


FIGURE 13. Plot of density of the IoNanofluids as a function of volume fraction. $\blacktriangle, \triangle$ – IoNanofluids based on $[\text{C}_2\text{mim}][\text{dca}]$; \blacklozenge, \lozenge – IoNanofluids based on $[\text{C}_4\text{mim}][\text{dca}]$; \blacksquare, \square – IoNanofluids based on $[\text{C}_4\text{mpyr}][\text{dca}]$, full symbols: experimental values; empty symbols: calculated values from equation (12).

[41], or if the CNT's are “empty” and therefore contribute with their intrinsic density according to the volume fraction in the fluid. In the first case the enhancement will be more discernible. More studies about the density of IoNanofluids are needed to clarify this point.

4. Conclusions

The thermophysical properties (thermal conductivity and density) of ionic liquids with a common anion, dicyanamide, and their IoNanofluids with multi-walled carbon nanotubes, were studied at temperatures between (293 and 343) K, at 0.1 MPa. The results obtained show that there are significant enhancements of the thermal conductivity caused by the suspension of this nanomaterial in the base liquid, which cannot be explained by current theories that do not consider the importance of the process of heat transfer in the interface ionic liquid – nanomaterial. On the other hand the enhancements in the density, to our knowledge the first results for IoNanofluids, are very small and not very dependent of the structure of the cation.

The results obtained help to understand the effect of the side alkyl chain, the planarity of the head group and the anion identity in the thermal conductivity of the ionic liquids and also in the respective IoNanofluids. Dicyanamide ionic liquids can be a good alternative for new heat transfer fluids, due to their low viscosity and to the enhancement in the thermal conductivity. Studies of the heat capacity and viscosity, the other two important thermophysical properties for heat transfer design are under way.

Molecular dynamics studies with real interaction potentials of interaction between the ionic liquid moieties and the carbon nanostructures will help to understand the true mechanism for thermal conductivity in ionic liquids and IoNanofluids, which we hope to report about soon.

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