

Thermal Properties of Ionic Liquids and Ionanofluids

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1. Introduction

The current world economy and energy situation demands the search for alternative energies to conventional fuels, the optimization of current energy technologies, and the search for new and clean working fluids. In the field of heat transfer, all current liquid coolants used at low and moderate temperatures exhibit very poor thermal conductivity and heat storage capacities, as the classical equipments for heat transfer use working fluids that were developed, tested and applied in a world of positive economical growth. In contrast, the uses of chemical technologies today are considered unsustainable. Although increased heat transfer can be achieved creating turbulence, increasing surface area and so on, ultimately the transfer will still be limited by the low thermal conductivity of the conventional fluids. Therefore, there is a need for new and efficient heat transfer liquids that can meet the cooling challenges for advanced devices as well as energy conversion for domestic and industrial applications.

Ionic liquids (IL) have proven to be safe and sustainable alternatives for many applications in industry and chemical manufacturing. Their success arises mainly from their thermophysical and phase-equilibria properties, and the versatility of their synthesis, manageable to be tailored for a given application. Their solvent properties as well as their heat transfer or heat storage and surface properties make this class of fluids possible to use in a high plethora of applications (Earle & Seddon, 2007; Nieto de Castro & Santos, 2007). Other advantages of ionic liquids include high ionic conductivity, high chemical and thermal stabilities, negligible vapor pressure and an ability to dissolve a wide range of inorganic and organic compounds. Due to all of these fascinating characteristics they have been investigated extensively as alternatives to molecular solvents for liquid phase reactions (Wasserscheid & Welton, 2007; Pârvulescu & Hardacre, 2007). Ionic liquids are of great interest to scientists as well as chemical companies, not only because of their interesting properties, but also for their actual and potential applications in the chemical process industries. In the past, the values of their thermophysical properties found to have significant effect on the design of physico-chemical processing and reaction units, influencing directly the design parameters and performance of equipments like heat exchangers, distillation columns and reactors (França et al., 2009). Their thermophysical properties justify the replacement of several of the chemical processes now under exploitation, and some of the solvents used, because they can, in certain conditions, be

considered as green solvents. However the optimal technological design of green processes requires the characterization of the ionic liquids used, namely their thermodynamic, transport and dielectric properties.

Thermophysical properties data of ionic liquids, that we can trust, not only because the samples are well purified and characterized, but also because the uncertainty of the data is well discussed, are needed for several applications and for the design of chemical plants. They can be obtained from experimental measurements, predictive or estimation techniques. Although there were some interesting developments in this last area, by using group contribution methods, the calculation of the thermophysical properties of ionic liquids with more or less theoretical based schemes is still very difficult, but useful for some properties (Gardas & Coutinho, 2009). Experiment, although not yet perfect, is still our main source of information. Recently, our group has reported few works (França et al., 2009; Nieto de Castro et al., 2010; Nunes et al., 2010) where experimental data on thermophysical properties of numerous ionic liquids are presented besides analyzing details of the situation of the values of these thermophysical properties, measurement methods and uncertainty as well as their potential applications including as heat transfer fluids.

The screening of all possibilities revealed in a recent review article (Murshed et al., 2008a) lead us to use nanofluids with ionic liquid as base fluids. Considering the fact that solid materials or particles, namely nanoparticles or carbon nanotubes (CNTs) have orders of magnitude higher thermal conductivity at room temperature than the base fluids, it has been shown that the thermal conductivity of fluids containing suspended particles (metallic, non-metallic) could be significantly higher than the base fluids (Murshed et al., 2008a). With this classical idea and applying nanotechnology to heat transfer, Steve Choi from Argonne National Laboratory of USA (Choi, 1995) coined the term "*nanofluid*" to designate a new class of heat transfer fluids which is formed by the dispersion of nanometer sized solid particles, rods or tubes in traditional heat transfer fluids such as water, ethylene glycol, and engine oil. From the investigations performed thereafter, nanofluids were found to have higher thermal conductivity and thermal diffusivity than those of the base fluids (Murshed et al., 2005, 2006 & 2008a). The suspensions or emulsions are stable and Newtonian, and these nanofluids have been proposed as 21st century heat transfer agents for cooling devices which respond more efficiently to the challenges of great heat loads, higher power engines and brighter optical devices, increased transportation, micromechanics, instrumentation, HVAC (heating, ventilating and air-conditioning) and medical applications (Das et al., 2006; Murshed et al., 2008a). Some researchers already considered these nanofluids to be the cooling media of the future (Das, 2006). Although significant progress has been made, variability and controversies in the heat transfer characteristics (Keblinski et al., 2008; Murshed et al., 2009) still exist which may be the result from the synthesis of the nanofluids being quite delicate. In fact, a nanofluid does not necessarily mean a simple mixture of nanoparticles and a liquid and the techniques used by different authors are sometimes ill-defined (Das, 2006; Murshed et al., 2008a).

Previous studies in nanofluids have used common liquids such as water, ethylene glycol or oils. No innovation has been made so far in the base fluids, until the work of (Nieto de Castro et al., 2010) where results for the thermal conductivity of several ionic liquids containing CNTs are presented. In addition to aforementioned advantages and applications, these liquids are also currently under intense study for chemical and materials processing, as environmentally friendly solvents and reaction fluids ("*green*" solvents) (Wasserscheid & Welton, 2007; Earle & Seddon, 2000; Nunes et al., 2010). These fluids are generally non-

flammable and non-volatile under ambient conditions and their thermophysical properties, being compatible with the requisites of heat transfer fluids, can be fine-tuned by their structure and tailored to satisfy the specific application requirements. According to the American National Renewable Energy Laboratory there have been no major developments in the field of thermal energy storage systems in the 1990's and the discovery of ionic liquids systems qualifies them as viable thermal fluids, a fact that is supported by recent applications as thermal fluids (Holbrey, 2007; França et al., 2009).

The discovery that carbon nanotubes and room-temperature ionic liquids can be blended to form gels that may be used to make novel electronic devices, coating materials, and antistatic materials, opens a completely new field (Fukushima et al., 2003; Fukushima & Aida, 2007). Blends or emulsions of ionic liquids with nanomaterials, mostly nanocarbons (tubes, fullerenes, and spheres) are termed as *Bucky gels*. The possibility of using ionic liquids containing dispersed nanoparticles with specific functionalization, for example single-walled nanotubes (SWCNTs), multi-walled nanotubes (MWCNTs) and fullerenes (C60, C80, etc.), opens the door to many potential applications. The use of nanoparticles as heat transfer enhancer allows us to associate small quantities of different types of nanomaterials to ionic liquids (i.e. ionanofluids), which are highly flexible such that they can be designed (target-oriented) in terms of molecular structure, to achieve the desired properties necessary to accomplish a given job. Complex systems based on nanomaterials and common solvents such as nanofluids proved to have thermophysical properties that can revolutionize the actual utilization of heat transfer fluids and heat storage cycles. This is mainly due to the existence of thermal conductivity enhancements derived from the presence of additional mechanisms of heat transfer, in comparison with the base solvent.

If nanoparticulates in any shapes and structures (e.g., spheres, cylinder or tubes) are dissolved or mixed as a thermally stable suspension in ionic liquids, "bucky gels" termed as "Ionanofluids" are formed. These ionanofluids have recently been found to have enhanced thermal conductivity ranging from 2 to 35%, and heat capacity compared to their base ionic liquids (Nieto de Castro et al., 2010; Ribeiro et al., 2010). Since these ionanofluids have fascinating features such as high thermal conductivity, high volumetric heat capacity and are non-volatile, they can potentially be used as novel heat transfer fluids.

Another fascinating area of application of the ionanofluids is their use in the development of new pigments for solar paint coatings, with high solar absorbance and the same thermal emissivity when compared with the base paint (Vieira et al., 2010), having a color different from black, with high importance in solar energy thermal conversion for architectural use. Preliminary work performed by this group, using carbon nanotubes, [C₄mim][PF₆] and crystal violet, showed a net gain in the paint efficiency (a_s/ϵ_T) of 0.45 to 0.57.

The purpose of this chapter is to present and analyze the most important thermal properties for an optimal technological design of process plants, namely thermal conductivity and heat capacity of ionic liquids and ionanofluids, from experimental data to molecular modeling of heat transfer and storage in these types of systems. Ionic liquids based on C_nmim cations and (CF₃SO₂)₂N, BF₄, PF₆ anions are used to illustrate the most important behaviors. The thermal conductivity and specific heat capacity data of several ionic liquids including 1-hexyl-3-methylimidazolium tetrafluoroborate, [C₆mim][BF₄], 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆], 1-hexyl-3-methylimidazolium hexafluorophosphate, [C₆mim][PF₆], 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [C₄mim][CF₃SO₃] and 1-butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide, [C₄mpyrr]((CF₃SO₂)₂N) and multi-walled carbon nanotubes (MWCNTs) ionanofluids as a

function of temperature are presented and discussed in this chapter. New results on the application of natural nanomaterials in heat transfer and storage are also presented.

2. Sample preparation and characterization

All ionic liquids used were synthesized and purified following the procedure given elsewhere (Bonhote et al., 1996; Holbrey et al., 2001). They were prepared through metathesis reactions from the appropriate $[C_n\text{mim}]\text{Cl}$. Prior to use samples were extensively washed using distilled water and dried overnight at 70 °C under high vacuum (0.1 Pa). Sample ionic liquids were analyzed by ^1H and ^{13}C NMR and elemental analysis. The water content was measured using Coulometric Karl-Fisher titration (Metrohm 831) before and after each measurement. In all cases, the water mass fraction was found to be less than 0.0002. The halide content of ionic liquids was determined using suppressed ion chromatography as described in (Villagran et al., 2004) and all ionic liquids had a chloride mass fraction of less than $5 \cdot 10^{-6}$, unless otherwise stated.

The carbon nanotubes used were Baytubes[®] C150 HP of Multi-Walled Carbon Nanotubes (MWCNTs) from Bayer Material Science (Germany). According to Bayer Material Science, the specifications of MWCNTs are given in Table 1. Baytubes[®] are produced from a high-yielding catalytic process based on chemical vapor deposition. The process yields easy to handle agglomerates with high apparent density. The optimized process results in a high degree of purity (low concentration of residual catalyst and absence of free amorphous carbon). Baytubes[®] are agglomerates of multi-wall carbon nanotubes with small outer diameters, narrow diameter distribution, and an ultra-high aspect ratio (length-to-diameter ratio). They show excellent tensile strength and E-modulus, as well as exceptional thermal and electrical conductivities. Aida and co-workers (Fukushima et al., 2003; Fukushima & Aida, 2007) found that imidazolium-ion-based ionic liquids were excellent dispersants for CNTs forming physical gels. Similar techniques were followed in this study to obtain very stable emulsions for 0.5 to 3% (w/w) loadings of MWCNTs (Sonicator Sonics & Materials, Model VC50) in various ionic liquids.

Property	Value	Unit	Method
C-Purity	> 99	%	Elementary analysis
Free amorphous carbon	Not detectable	%	TEM
Number of walls	3-15	-	TEM
Outer mean diameter	13-16	nm	TEM
Outer diameter distribution	5-20	nm	TEM
Inner mean diameter	4	nm	TEM
Inner diameter distribution	2-6	nm	TEM
Length	1-10	μm	SEM
Bulk density	140-230	$\text{kg}\cdot\text{m}^{-3}$	EN ISO 60

Table 1. Specifications of Baytubes[®] product used

Figure 1 shows the ionanofluid for $[C_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}] + 0.5\%(\text{w/w})$ MWCNTs. The liquid is black, coloured by the Baytubes[®], and viscous. The gel is stable but special care is to be taken in its production.



Fig. 1. Filling a thermal conductivity cell with the ionanofluid $[\text{C}_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}] + 0.5\%(\text{w/w})$ MWCNTs.

3. Experimental details

In this study, a KD2 Pro Thermal Properties Analyzer (Labcell Ltd., UK) was used to measure the thermal conductivity of sample fluids. The measurement principle of KD2 is based on the transient hot-wire technique. Instead of using a bare wire, an electrically isolated thermal probe coated with a thin coating of an insulator is used as the ionic liquids are electrically conducting liquids (Ramires et al., 1994; Chen et al., 2008; Nunes et al., 2010). The thermal probe of this KD2 analyzer has 1.3 mm diameter and 60 mm length and contains both the heating element and thermoresistor. This probe should be inserted into the sample vertically, rather than horizontally, to minimize the possibility of inducing convection. The measurement is made by heating the probe within the sample while simultaneously monitoring the temperature change of the probe. A microprocessor connected to the probe is used to control the heating rate and to measure the temperature change data. The thermal conductivity is then calculated based on a parameter-corrected version of the transient temperature model given by Carslaw and Jaeger (Carslaw & Jaeger, 1959) for an infinite line heat source with constant heat output and zero mass in an infinite medium. For this model to accurately describe the physical behavior of a system, the heat source must closely approximate an infinitely long and as thin as possible wire. This KD2 analyzer used the solutions for a heated cylindrical source with a non-negligible radius and finite length as described by Kuitenberg and co-workers (Kuitenberg et al., 1993). Both models give good fit to the temperature data but differ slightly in value of the fitting parameters and these differences can be accounted for by the careful calibration allowing

the former (simpler also) model to be widely used and it has been employed herein (Chen et al., 2008). Before and after analysis of the sample liquids, the meter was calibrated using water and a standard sample of glycerol of known thermal conductivity. Approximately 15 cm³ of the sample to be analyzed was sealed in a glass sample vial. The probe was inserted vertically into the sample via a purpose-made port in the lid of the vial. The sealed vial was then fully immersed in a temperature-controlled water bath (Grant GD120) which allowed equilibrating at the desired temperature of the test sample. Once the sample reached the required temperature, a further 15 min was allowed to pass before carrying out the measurement to ensure complete temperature equilibration and stability. At least four measurements were taken at each temperature, with a delay of at least 15 min between each measurement, to ensure reproducibility. More details about the measurement procedure can be found in a work (Ge et al., 2007) where KD2 Pro device was also used to measure thermal conductivity of several ionic liquids. Based on the standard deviations of experimental and calibration data, the uncertainty of the thermal conductivity and temperature measurements were estimated to be $\pm 0.005 \text{ Wm}^{-1} \text{ K}^{-1}$ and $\pm 1 \text{ K}$, respectively.

On the other hand, the heat capacity measurements were performed with a differential scanning calorimeter (DSC-111, Setaram, France) which was calibrated in enthalpy (Joule effect) and temperature following the procedure described by (Nieto de Castro et al., 2000; ; Lourenço et al., 2006). This calorimeter is a heat-flux DSC which operates based on the Tian-Calvet principle and uses a cylinder type measuring system composed by two sintered alumina cylinder tubes. These tubes are set parallel to each other in the heating furnace. The sensing part of this calorimeter is the central portion of the cylinders and thermocouple-carrying heat-flux transducers (thermopiles) are wrapped around this central portion. The heat flow can then be measured by the temperature changes in these transducers. Details of the experimental procedure and calibration of this DSC can be found elsewhere (Nieto de Castro et al., 2000; Lourenco et al., 2006) and will not be elaborated here. In this study, the melting temperatures of Hg, Ga, In, Sn, Pb and Zn were used to calibrate the temperature as indicated in the instrument user manual and the heat of fusion of these metals was used to assess the calibration uncertainty due to the Joule effect. Table 2 shows the reference materials used, their origin and purity, as well as the recommended values for the enthalpies and temperatures of fusion. Calibration materials used were chosen from the published references as well as from the Certified Reference Materials Certificate (CRMC) – LGC (UK). Results obtained for the melting (fusion) temperatures and fusion enthalpies of the Hg, Ga, In, and Sn are shown in Table 3. The uncertainty in the enthalpy measurements was found to be of the order of 1%, while the temperature measurements agree within 0.1 K with the standard values, except for mercury, where data only at 2 K min⁻¹ was determined. The heat capacity was obtained using closed stainless steel crucibles, by continuous method-standard zone, with a scanning rate of 2 K min⁻¹ (Setaram SETSOFT 2000, Version 3.0). The mass of the samples was confirmed after each run to check any possible weight losses. The heat capacity was determined from the total energy detected by the calorimeter i.e. $(Q_p)_{meas}$, the calibration constant, K , and the scanning rate β using the following equation:

$$C_p = \frac{(Q_p)_{meas}}{K \cdot \beta} \quad (1)$$

Reference Material	Origin	Purity (%)	T_{fus}/K	$\Delta_{fus}H_m / J mol^{-1}$	Reference
Hg	BDH	> 99.999	234.29 ± 0.01	2295.3 ± 0.8	(Sabbah et al., 1999)
Ga	Alfa Chemicals	99.999	302.915 302.92 ± 0.02	5569 ± 50 5590 ± 40	(Thomas, 1990) (Chase, 1998)
In	LGC 2601	99.999	429.76 ± 0.02	3296 ± 9	CRMC
Sn	LGC 2609	99.999	505.07 ± 0.02	7187 ± 4	CRMC
Pb	LGC 2608	99.996	600.62 ± 0.02	4756 ± 11	CRMC
Zn	LGC 2611	99.996	692.68 ± 0.02	7103 ± 31	CRMC

Table 2. Reference materials used for the temperature calibration

	Hg (Bi-distilled)	Ga	In	Sn
$(\Delta_{fus}H)_{std} / J mol^{-1}$	2295.3 ± 0.8 (Sabbah et al., 1999; Chase, 1998)	5569 ± 60 (Sabbah et al., 1999) 5590 ± 40 (Chase, 1998)	3296 ± 9	7187 ± 4
$(\Delta_{fus}H)_{exp} / J mol^{-1}$	2268 ± 33	5568 ± 71	3249 ± 35	7083 ± 74
T_{std} / K	234.29 ± 0.01 (Thomas, 1990; Sabbah et al., 1999)	302.92 ± 0.02 (Chase, 1998), 302.915 (Thomas, 1990)	$429.76 \pm$ 0.02	$505.07 \pm$ 0.02
T_{exp} / K	233.58 ± 0.19 (at 2 K min ⁻¹) -	- 303.08 ± 0.29^a	$429.68 \pm$ 0.07 $429.66 \pm$ 0.02 ^a	$505.01 \pm$ 0.07 $505.16 \pm$ 0.15 ^a

^a Extrapolation to zero scanning rate

Table 3. Comparison between the temperature and enthalpy of fusion of mercury, gallium, indium (LGC 2601) and tin (LGC 2609).

After calibration, the measurement technique of specific heat of sample fluids composed of a double experiment performing two nearly identical runs—one with the two cells without sample and the other with the sample in one of the cells. In this way, any differences between the two crucibles are eliminated from the final signal to be used in equation (1). The uncertainty of the heat capacity determinations is found to be better than 1.5% at a 95% confidence level. It is noted that according to the ISO definition, a coverage factor $k=2$ is used and in order to obtain the accuracy value it must be divided by 2 (Sampaio & Nieto de Castro, 1998). We have checked the accuracy of the measurements by measuring the heat capacity of certified reference material sapphire (NIST SRM-707), between room temperature and 430 K, and found deviations of less than 1.5 % with an average absolute deviation (AAD) of 0.68%.

4. Results and discussions

4.1 Thermal conductivity of ionic liquids and ionanofluids

The thermal conductivity of [C₆mim][BF₄], [C₄mim][PF₆], [C₆mim][PF₆], [C₄mim][CF₃SO₃], and [C₄mpyrr][(CF₃SO₂)₂N] were measured for various temperature ranging from 293 K to 353 K and at 0.1 MPa. Figure 2 shows the results obtained from this study. It can be seen that the thermal conductivity variation with temperature is linear and that no data point departs from linearity by more than ±0.6%. A linear correlation used to fit the results is expressed by equation (2). Table 4 depicts the coefficients of regression for equation (2) and the root mean square deviations of the fits. The variance of the fits do not exceed 0.48 mW m⁻¹ K⁻¹, about 0.3%.

$$\lambda \left(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \right) = a_1 + a_2 (T / \text{K}) \quad (2)$$

Few similar studies from literature on ionic liquids are also reported here as their results are compared with the present results. Using the transient short-hot-wire method with an uncertainty of 2-4% (Tomida et al., 2007) measured the thermal conductivity of [C₄mim][PF₆], and [C₆mim][PF₆] from temperature between 294 K and 335 K and at pressure up to 20 MPa. Their samples were synthesized, dried by heating in a vacuum and purified by adsorbing the impurities onto activated charcoal. Therein, the water content after the measurements was found to be in the range 70-90 ppm. (Ge et al., 2007) reported measurements for [C₄mpyrr][(CF₃SO₂)₂N] and [C₄mim][CF₃SO₃] using the same instrument presented in this work, with an estimated uncertainty of ± 0.005 W m⁻¹ K⁻¹. The water content was found to be less than 80 ppm and the chloride mass fraction was less than 5 · 10⁻⁶.

Ionic Liquids and Ionanofluids	$a_1 \pm \sigma_{a1}$ / W m ⁻¹ K ⁻¹	$10^4(a_2 \pm \sigma_{a2})$ / W m ⁻¹ K ⁻²	σ / W m ⁻¹ K ⁻¹
[C ₆ mim][BF ₄]	0.19379 ± 0.00179	-1.214 ± 0.053	0.00029
[C ₄ mim][CF ₃ SO ₃]	0.16149 ± 0.00248	-0.679 ± 0.077	0.00041
[C ₄ mpyrr][(CF ₃ SO ₂) ₂ N]	0.12699 ± 0.00313	-0.300 ± 0.100	0.00032
[C ₄ mim][PF ₆]	0.15784 ± 0.00253	-0.429 ± 0.078	0.00041
[C ₆ mim][PF ₆]	0.16279 ± 0.00292	-0.714 ± 0.090	0.00048
[C ₆ mim][BF ₄] + MWCNT	0.17631 ± 0.00179	-0.357 ± 0.006	0.00029
[C ₄ mim][CF ₃ SO ₃] + MWCNT	0.16310 ± 0.00200	-0.321 ± 0.006	0.00032
[C ₄ mpyrr][(CF ₃ SO ₂) ₂ N] + MWCNT	0.13279 ± 0.00313	-0.300 ± 0.010	0.00032
[C ₄ mim][PF ₆] + MWCNT	0.16501 ± 0.00372	-0.500 ± 0.115	0.00061
[C ₆ mim][PF ₆] + MWCNT	0.15844 ± 0.00179	-0.500 ± 0.055	0.00029

Table 4. Coefficients of equation (2) for ionic liquids and ionanofluids (1wt.% of MWCNTs)

Figure 3 demonstrates the deviations of our data as well as data from literature from equation (2). It can be seen that none of our data point deviated from the linear fitting by more than 0.5%. In addition, the deviations from our fits of the data from (Ge et al., 2007) for [C₄mpyrr][(CF₃SO₂)₂N] and [C₄mim][CF₃SO₃], and by (Tomida et al., 2007) for [C₄mim][PF₆], and [C₆mim][PF₆], obtained using a bare platinum wire are also shown in Figure 3. In all cases, the data agree within the errors associated with the methods used. It can also be seen that both sets of literature data (Ge et al., 2007; Tomida et al., 2007) are slightly higher than those of our data which may be associated with higher purity samples

utilized in the present study. (Ge et al., 2007) showed that small levels of water or halide, which are common impurities from the synthesis of ionic liquids, both increase the thermal conductivity of ionic liquids.

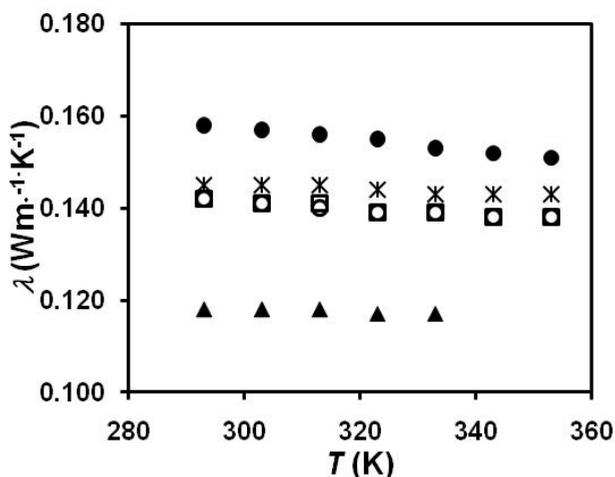


Fig. 2. Thermal conductivity of ionic liquids as a function of temperature (legends: ● - [C₆mim][BF₄]; ○ - [C₄mim][CF₃SO₃]; ▲ - [C₄mpyrr][((CF₃SO₂)₂N)]; * - [C₄mim][PF₆]; □ - [C₆mim][PF₆]).

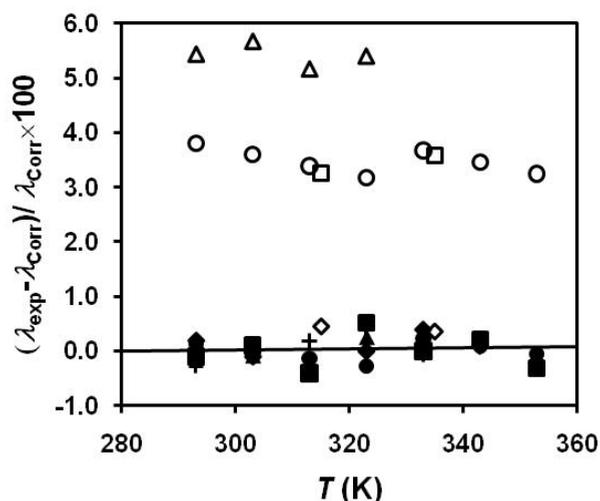


Fig. 3. Deviations between our data and other data from equation (2), as a function of temperature (legends: ● - [C₆mim][BF₄]; + - [C₄mim][CF₃SO₃]; ▲ - [C₄mpyrr][((CF₃SO₂)₂N)]; ◆ - [C₄mim][PF₆]; ■ - [C₆mim][PF₆]; △ - C₄mpyrr][((CF₃SO₂)₂N)] from (Ge et al., 2007); ○ - [C₄mim][CF₃SO₃] from (Ge et al., 2007); ◇ - [C₄mim][PF₆] from (Tomida et al., 2007); □ - [C₆mim][PF₆] from (Tomida et al., 2007)).

The thermal conductivities of the ionanofluids produced by dispersing MWCNTs in [C₆mim][BF₄], [C₄mim][PF₆], [C₆mim][PF₆], [C₄mim][CF₃SO₃] and [C₄mpyrr][((CF₃SO₂)₂N)] were measured at various temperatures between 293 K and 353 K and at 0.1 MPa. Thermal conductivity data obtained for these new ionanofluids are presented. Figure 4 shows the measured thermal conductivity of various ionanofluids as a function of temperature and at constant concentration of MWCNTs (1 wt. %). Some of the ionanofluids show a temperature dependent enhancement ([C₆mim][BF₄] and [C₄mim][CF₃SO₃]), while the remaining ionanofluids demonstrate a constant increase (5% for [C₄mpyrr][((CF₃SO₂)₂N)], 3.4% for [C₄mim][PF₆], and 1.8% for [C₆mim][PF₆]). Like ionic liquids, the thermal conductivity variation is linear with temperature and that no data point departs from linearity by more than ±0.25%. The coefficients of regression for equation (2) and the root mean square deviations of the fits are given in Table 4.

Results of temperature-dependent thermal conductivity enhancements of these ionanofluids ($\lambda_{\text{ionanofluids}}/\lambda_{\text{IL}}$) are also presented in Figure 5. The natures of the enhancements of thermal conductivity of these ionanofluids are somewhat similar to previously reported enhancements for other nanofluids (Murshed et al, 2008a). In general, ionanofluids containing [PF₆]⁻ based ionic liquids have the smallest enhancement in thermal conductivity whilst those based on [C₆mim][BF₄] had the largest (9% on average) change. No smooth dependence on the cations or anions was found. Similar dependency was also recently observed for the [C_nmim]⁺ -based ionic liquids in another study by our group (Ribeiro et al., 2010).

The interpretation of the thermal conductivity enhancement in particle suspensions such as nanofluids has been the object of many publications, since the pioneering work of Maxwell (Maxwell, 1891). This Maxwell's model was developed for millimeter and micrometer sized particles suspended in liquids, and the ratio between the thermal conductivity of the nanofluid and that of the base fluid, $\lambda_{\text{NF}}/\lambda_{\text{BF}}$, was found to depend on the thermal conductivity of both phases (solid and liquid) and on the volume fraction of the solid. This model, adapted for the ionanofluids is given as

$$\frac{\lambda_{\text{NF}}}{\lambda_{\text{IL}}} = \frac{\lambda_{\text{CNT}} + 2\lambda_{\text{IL}} + 2\phi_{\text{CNT}}(\lambda_{\text{CNT}} - \lambda_{\text{IL}})}{\lambda_{\text{CNT}} + 2\lambda_{\text{IL}} - \phi_{\text{CNT}}(\lambda_{\text{CNT}} - \lambda_{\text{IL}})} \quad (4)$$

where λ_{NF} , λ_{IL} , λ_{CNT} are, the thermal conductivity of nanofluid, ionic liquid, and carbon nanotubes (CNT), respectively. ϕ_{CNT} is the volume fraction of CNTs.

In order to incorporate the shape of the particles (e.g. cylinders) and the interaction between the particles, extensions of this Maxwell model were later developed by (Hamilton and Crosser, 1962) and (Hui et al., 1999). However, these classical models were found to be unable to accurately predict the anomalously high thermal conductivity of nanofluids (Murshed et al., 2008a). Thus, researchers have proposed several mechanisms to explain this phenomenon. For example, (Kebblinski et al., 2002) systematized the four different mechanisms for heat transfer to explain these enhancements, namely (i) Brownian motion of the nanoparticles (ii) liquid layering at the liquid/particle interphase, (iii) the nature of the heat transport in the nanoparticles and (iv) the effect of nanoparticle clustering. From the analysis made in an exhaustive review paper on nanofluids (Murshed et al., 2008a) and other publications cited, therein, it is our belief that the effect of the particle surface chemistry and the structure of the interphase particle/fluid are the major mechanisms responsible for the unexpected enhancement in nanofluids.

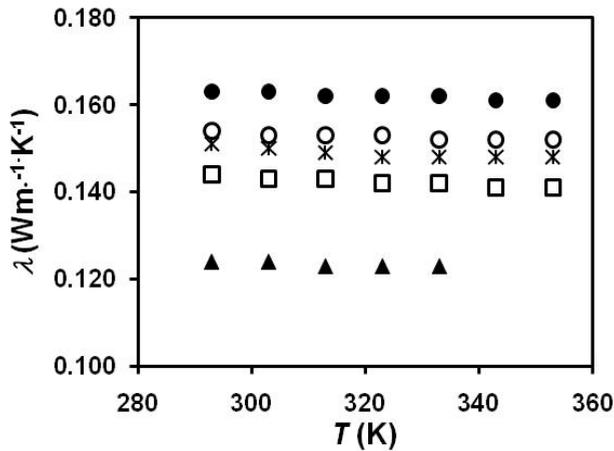


Fig. 4. Thermal conductivity of ionanofluids as a function of temperature for 1 wt% loading of MWCNTs (legends: ● - $[\text{C}_6\text{mim}][\text{BF}_4] + \text{MWCNTs}$; ○ - $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] + \text{MWCNTs}$; ▲ - $[\text{C}_4\text{mpyr}][(\text{CF}_3\text{SO}_2)_2\text{N}] + \text{MWCNTs}$; * - $[\text{C}_4\text{mim}][\text{PF}_6] + \text{MWCNTs}$; □ - $[\text{C}_6\text{mim}][\text{PF}_6] + \text{MWCNTs}$)

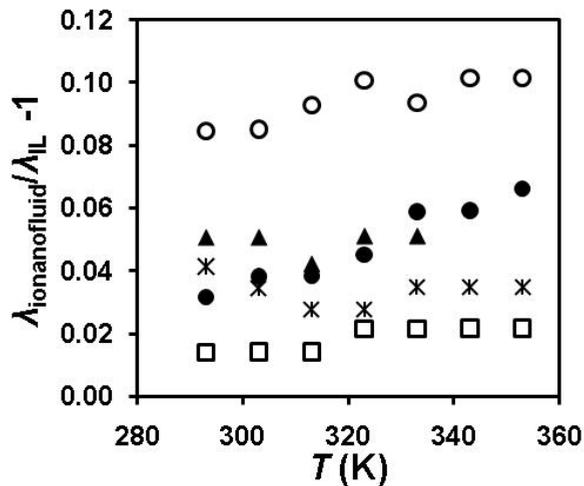


Fig. 5. Thermal conductivity enhancement in the ionanofluids with a loading of 1 wt% of MWCNTs (legends: ● - $[\text{C}_6\text{mim}][\text{BF}_4] + \text{MWCNTs}$; ○ - $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3] + \text{MWCNTs}$; ▲ - $[\text{C}_4\text{mpyr}][(\text{CF}_3\text{SO}_2)_2\text{N}] + \text{MWCNTs}$; * - $[\text{C}_4\text{mim}][\text{PF}_6] + \text{MWCNTs}$; □ - $[\text{C}_6\text{mim}][\text{PF}_6] + \text{MWCNTs}$)

Incorporating some of the key mechanisms, Murshed and co-workers (Leong et al., 2006; Murshed et al., 2008b) solved the heat transfer equation for spherical and infinitely long cylinders for three-phase systems (particle, interfacial layer and base fluids) and developed two models for the effective thermal conductivity of nanofluids containing spherical and

cylindrical nanoparticles. Besides particle concentration and thermal conductivity of each phase, these models take into account the effect of particle size, and interfacial nanolayer between particle and the base fluids. The thermophysical properties of the interfacial layer are considered to be different from those of the bulk liquid and of the solid particles. In this study, one of these models for cylindrical particles (Murshed et al., 2008b) was used for the determination of the effective thermal conductivity of ionanofluids containing CNTs in various ionic liquids. The model is expressed as

$$\lambda_{NF} = \frac{(\lambda_{CNT} - \lambda_{Int})\phi_{CNT}\lambda_{Int}\left[2\gamma_1^2 - \gamma^2 + 1\right] + (\lambda_{CNT} + 2\lambda_{Int})\gamma_1^2\left[\phi_{CNT}\gamma^2(\lambda_{Int} - \lambda_{LI}) + \lambda_{LI}\right]}{\gamma_1^2(\lambda_{CNT} + 2\lambda_{Int}) - (\lambda_{CNT} - \lambda_{Int})\phi_{CNT}\left[\gamma_1^2 + \gamma^2 - 1\right]} \quad (5)$$

where

$$\gamma = 1 + \frac{h}{a} \quad \text{and} \quad \gamma_1 = 1 + \frac{2h}{a} \quad (6)$$

In these equations (5) and (6), λ_{IP} is the thermal conductivity of the interphase, a is the radius of the cylinder and h the thickness of the interfacial layer (nanolayer at the CNT-IL interface). It should be noted that there is no exact theoretical model to determine h ; however, (Murshed et al., 2008b) showed that this parameter is not critical and in the present calculations we used $h \approx 2$ nm as used by (Murshed et al., 2008b) for CNTs-nanofluids. In addition, as no values of λ_{IP} exist for IL/CNTs systems, we have used λ_{IP} as an adjustable parameter, keeping in mind that its value will be, in principle, intermediate between the values of λ_{IL} and λ_{CNT} . (Murshed et al., 2008b) found $\lambda_{IP} = 60 \lambda_{IL}$ for ethylene glycol/CNTs nanofluids.

Table 5 shows the results obtained for the ionanofluids studied. It also compares the experimentally observed enhancement ($\lambda_{NF}/\lambda_{IL}-1$) with the values predicted from Maxwell model (Maxwell, 1891) and Murshed et al.'s model (Murshed et al., 2008b). In the prediction, an average value of $a = 7.5$ nm was used for the MWCNTs and a value of $\lambda_{CNT} = 2000 \text{ W m}^{-1} \text{ K}^{-1}$ (Choi et al., 2001) was assumed, as no other information regarding the value for the Baytubes® exists. Calculations were performed for 293 K, as the temperature dependence of the thermal conductivity of both the ionic liquids and the ionanofluids is small. Values for the density of the ionic liquids were obtained from the ILThermo database (NIST Standard Reference Database #147). The limiting value of Maxwell model, for volume fractions that oscillate between 0.6 and 0.7 is approximately 1.2, depending also slightly of the thermal conductivity of the ionic liquid. As equation (4) is the limiting value of equation (5), applying equation (5) to these systems, values of $\lambda_{IP}=0$, and $h=0$ were obtained, and it predicts a value of the thermal conductivity enhancement greater than found for all the systems studied. Only for systems where the enhancement is of the order of 20% or greater can the theory describe the effect of the thermal conductivity of the interface solid/liquid, as found for $[\text{C}_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ (Ribeiro et al., 2010).

In terms of volume, we have occupancy of 6% of the nanotubes. This might suggest that the ionanofluids consist the same type of nanostructural organization found by (Lopes & Padua, 2006) using molecular dynamics simulations for $[\text{C}_n\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ and $[\text{C}_n\text{mim}][\text{PF}_6]$ ionic liquids. They reported that for ionic liquids with alkyl chains where $n \geq 4$, aggregation of the alkyl chains into nonpolar domains was observed. This creates a tridimensional

Base Ionic Liquid	$\rho / \text{kg m}^{-3}$	$\lambda_{\text{IL}} / \text{W m}^{-1} \text{K}^{-1}$	w_{CNT}	ϕ_{CNT}	$\lambda_{\text{NF}} / \lambda_{\text{IL}} - 1$		
					Experimental	Eq. (4)	Eq. (5)
[C ₆ mim][BF ₄]	1148	0.158	0.01	0.0590	0.048	0.19	0.19
[C ₄ mim][CF ₃ SO ₃]	1306	0.142	0.01	0.0666	0.094	0.21	0.22
[C ₄ mpyrr][[(CF ₃ SO ₂) ₂ N]	1454	0.118	0.01	0.0735	0.049	0.24	0.25
[C ₄ mim][PF ₆]	1372	0.145	0.01	0.0697	0.034	0.22	0.23
[C ₆ mim][PF ₆]	1298	0.142	0.01	0.0662	0.018	0.21	0.22

Table 5. Thermal conductivity enhancement in the ionanofluids studied ($T=293 \text{ K}$)

network of ionic channels formed by the anions and the imidazolium rings of the cations and provides evidence of microphase separation between polar and non-polar domains within the liquid phase structure. The CNTs dispersed in the ionic liquid are likely to interact preferentially with the non polar domains associated with the alkyl chains, therefore creating microclusters that will enhance the heat transfer. However, as the length of the nanotubes (commonly 1-10 μm) is significant, the structure of the ionanofluids is likely to be different compared with that of the base fluid.

The enhanced thermal conductivity of the ionanofluids is consistent with previous studies involving metal nanoparticles in molecular solvents such as water or ethylene glycol (Choi et al., 2001; Murshed et al., 2008b). The strong interaction between the ionic liquid and CNTs has been demonstrated by (Fukushima et al., 2003; Fukushima & Aida, 2007) wherein the ionanofluids containing highly exfoliated CNT bundles were found to be less entangled after mixing. These bundles form a network structure that will indeed increase the thermal conductivity (an effect similar to aggregation) by creating privileged paths for heat conduction.

4.2 Heat capacity of ionic liquids and ionanofluids

Measurements of the heat capacity were performed at 0.1 MPa, and temperatures between 308 and 423 K and the results obtained for [C₄mim][BF₄] and [C₄mim][PF₆] ionic liquids are presented in Table 6. The experimental values were fitted as a function of temperature with the polynomial given as.

$$C_p \left(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \right) = b_1 + b_2 (T / \text{K}) + b_3 (T / \text{K})^2 \quad (7)$$

Table 7 shows the coefficients of regression for equation (7) and the root mean square deviations associated with the fits for [C₄mim][BF₄] and [C₄mim][PF₆]. While the variance for [C₄mim][BF₄] is 0.914 J mol⁻¹ K⁻¹, approximately 0.3 %, the variance for [C₄mim][PF₆] is 1.29 J mol⁻¹ K⁻¹, approximately 0.3 %. Figure 6 shows the variation of heat capacity with temperature, together with the results obtained by various research groups (Rebelo et al., 2004; Kim et al., 2004; Fredlake et al., 2004; Waliszewski et al., 2005; Van Valkenburg et al., 2005; Garcia-Miaja et al., 2008 & 2009). All these data were obtained with DSC. A wide variation between the datasets of up to 20 % at room temperature is observed. This situation is very uncommon in calorimetry; however it is known that, apart from differences in sample purity, the DSC used must be well calibrated and this may explain the scatter of data.

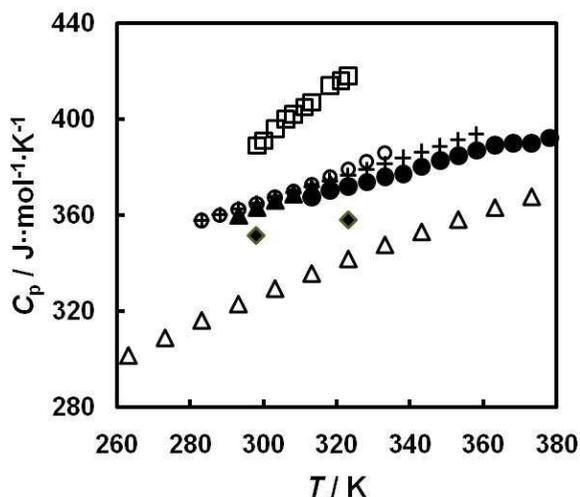
Figure 7 shows the variation of heat capacity with temperature together with the results obtained from various research groups (Holbrey et al., 2003; Kabo et al., 2004; Fredlake et al.,

T/K	$C_p / \text{J mol}^{-1} \text{K}^{-1}$	
	[C ₄ mim][BF ₄]	[C ₄ mim][PF ₆]
308.16	367.26	410.64
318.16	370.39	417.74
328.22	373.73	423.43
338.19	377.15	429.11
348.25	382.69	436.22
358.25	386.99	441.90
368.17	390.00	444.74
378.20	392.18	450.43
388.20	395.28	457.53
398.20	397.93	463.21
408.16	403.88	470.32
418.19	404.98	473.16
423.22	406.62	474.58

Table 6. Heat capacity of [C₄mim][BF₄] and [C₄mim][PF₆] as a function of temperature

Ionic Liquid	$b_1 \pm \sigma_{b1}$ / $\text{J mol}^{-1} \text{K}^{-1}$	$b_2 \pm \sigma_{b2}$ / $\text{J mol}^{-1} \text{K}^{-2}$	$10^4 (b_3 \pm \sigma_{b3})$ / $\text{J mol}^{-1} \text{K}^{-3}$	σ / $\text{J mol}^{-1} \text{K}^{-1}$
[C ₄ mim][BF ₄]	177.989 ± 23.134	0.80054 ± 0.12732	-6.1596 ± 1.7393	0.9140
[C ₄ mim][PF ₆]	182.288 ± 32.828	0.87307 ± 0.18067	-4.2115 ± 2.4681	1.2933

Table 7. Coefficients of equation (7)

Fig. 6. Comparison of present results and data obtained from literature for heat capacity of [C₄mim][BF₄] as a function of temperature (legends: ● - Present work; ○ - Rebelo et al., 2004; □ - Kim et al., 2004; ◆ - Fredlake et al., 2004; + - Waliszewski et al., 2005; △ - Van Valkenburg et al., 2005; * - Garcia-Miaja et al., 2008; ▲ - Garcia-Miaja et al., 2009)

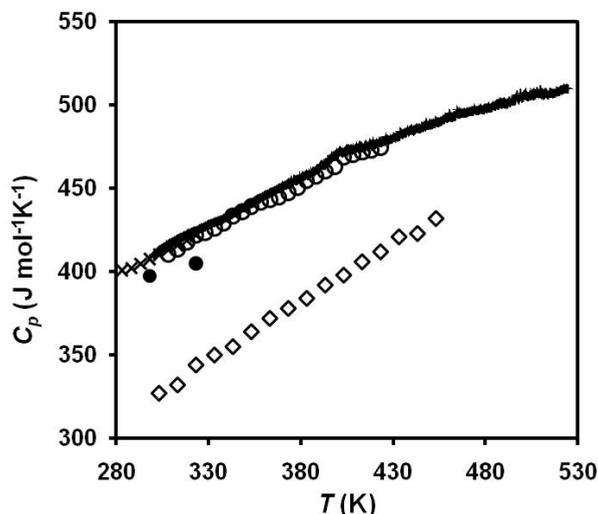


Fig. 7. Comparison of present heat capacity data of $[C_4mim][PF_6]$ with results from literature as a function of temperature (legends: \circ - Present work; \diamond - Holbrey et al., 2003; $+$ - Kabo et al., 2004; \bullet - Fredlake et al., 2004; \times - Troncoso et al., 2006)

2004; Troncoso et al., 2006). With the exception of the data reported by Kabo and co-workers (Kabo et al., 2004) which were obtained using a heat bridge calorimeter, all the remaining data were obtained using DSC. Our data agrees with the data of (Troncoso et al., 2006) between 0.4 and 0.6% and with (Kabo et al., 2004) between 0.8% and 1.2%. Results with deviations greater than $\pm 2\%$ are not included. Although data reported in this study are slightly lower, these variations are within the expected uncertainty of the data in all cases. In contrast, the data reported by (Fredlake et al., 2004) and especially those reported by (Holbrey et al., 2003) are much lower than our data with the latter data showing deviations of up to -20%.

The possible use of ionic liquids as heat transfer fluids, for heat exchange in chemical plants and solar thermal power generation, from cryogenic temperatures up to 200 °C, is based on the values of heat capacity per unit volume, very low vapor pressures, wide liquid ranges, thermal stability (some can be used at temperatures up to 500 °C) has been discussed (Holbrey et al., 2003), and its comparison with the properties of synthetic compounds (based on hydrocarbons, polyaromatics and siloxanes), showed that common imidazolium systems have higher heat capacities per unit volume than two high performance commercial thermal fluids, Paratherm HE[®] and Dowtherm MX[™], in all the applicable temperature range. This analysis was complemented (França et al., 2009; Nieto de Castro, 2010a) for several ionic liquids and Syltherm 800[™], Syltherm HF[™] and Dowtherm A[™] (trademarks of Dow Chemical Company, USA) as well as Paratherm HE[®] (registered mark of Paratherm Corporation). Figure 8 demonstrates the results obtained for various ionic liquids such as $[C_4mim][CF_3SO_2)_2N]$, $[C_2mim][C_2H_5SO_4]$, $[C_4mim][dca]$ and $[Aliquat\ 336^{®}\text{-derived}][dca]$ together with data for several commercial heat transfer fluids. It is clear that the heat capacities per unit

volume (ρC_p) of these ionic liquids are 20-40% higher than those of commercial heat transfer fluids in the temperature range studied. The same happens with other ionic liquids (França et al., 2009). These results are highly promising if we use these biodegradable and green ionic liquids in ionanofluids for their numerous potential applications.

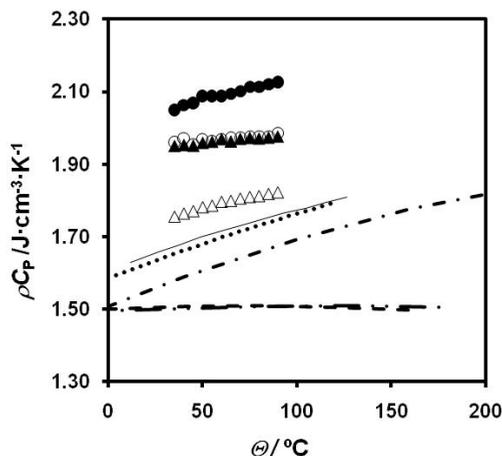


Fig. 8. Temperature-dependent heat capacity per unit volume for the ionic liquids and several heat transfer fluids (legend: \blacktriangle - $[\text{C}_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$; \bullet - $[\text{C}_2\text{mim}][\text{C}_2\text{H}_5\text{SO}_4]$; \circ - $[\text{C}_4\text{mim}][\text{dca}]$; \triangle - $[\text{Aliquat 336}^{\text{®}}\text{-derived}][\text{dca}]$; ---Syltherm800TM; ---- Syltherm HFTM; — Dowtherm ATM; - - - Dowtherm MXTM; Paratherm HE[®]). Data for the heat transfer fluids are obtained from their Material Safety Data Sheets which are available on-line.

The heat capacity of $[\text{C}_4\text{mim}][\text{PF}_6]$ -based ionanofluid was measured for two different concentrations of MWCNTs (1 wt.% and 1.5 wt.%) and the results are shown in Figure 9. The results are very surprising, as a large maximum in the heat capacity as a function of temperature is found compared with the bulk ionic liquid. Interestingly, around temperature between 350 to 375K, a jump in heat capacity of ionanofluids was observed (Figure 9) and the reason for such behavior is not known at this moment. Similar data has not been reported previously for nanofluids. Figure 10 depicts the heat capacity enhancement of ionanofluids ($C_{p,\text{NF}}$) over base ionic liquid ($C_{p,\text{IL}}$) i.e. $C_{p,\text{NF}}/C_{p,\text{IL}}-1$ as a function of temperature. The maximum enhancement observed, shaped as a dome as in critical behavior in pure fluids and near immiscibility critical end points, is clear and shows a peak of 8% compared with the bulk liquid irrespective of the CNT loading. Some noise, within the accuracy of the measurements, is found at the lower and higher temperatures. Further investigations using other ionic liquids and the application of phenomenological theories of criticality are to be performed in order to understand the interactions involved in these systems and to examine whether the aggregation phenomena or nanostructural organization exhibited are important in the mechanisms of the effects observed.

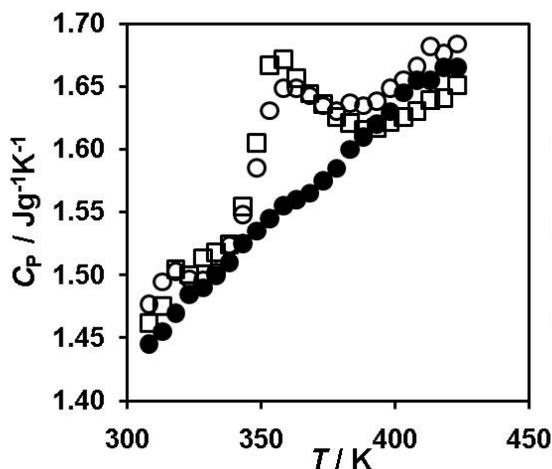


Fig. 9. Heat capacity of $[C_4mim][PF_6]$ -based ionanofluid for two different MWCNTs loadings as a function of temperature (legends: ● - $[C_4mim][PF_6]$; □ - $[C_4mim][PF_6]$ + 1 wt% of MWCNTs; ○ - $[C_4mim][PF_6]$ + 1.5 wt% of MWCNTs). The data are expressed in mass units as the molecular weight of the MWCNTs is not known.

5. Natural nanomaterials and their potential in ionanofluids

Natural nanomaterials open a completely new field in heat transfer as they have unusual thermal properties derived from its structure. It is in principle possible to use natural products from the biosphere, marine or plant origin, to be used as heat transfer enhancers. There is a plethora of materials, all renewable and biodegradable that can be tested and their thermal properties are to be determined. From the present knowledge some of them are already applied in domestic application like cherry stones and grape seeds, whereby several minutes of heating in a microwave oven can be sufficient to heat a fleece bag of these seeds to 70°C and let it last for several hours at 50°C, a self kept warming pillow. This result is quite surprising and can only be explained by the structure of the cherry stones.

Figure 11 presents FEG-SEM images obtained from a JEOL JSM-7001F equipment for cherry stone bits, produced by grinding the cherry stones down to grains of 200 μm average diameter, with four different magnifications i.e., 200x, 650x, 1400x and 7500x (also shown on images) (Queirós, 2010). The structure of the surface and of the pores is completely visible. It is very clear that the surface of the material has micropores (dimensions around 10 μm), but these micropores have nanopores smaller than 1 μm , like ice cream cone shape. These pores can not only trap gases inside and increase the thermal conductivity and the heat capacity, but also they can accommodate ionic liquid molecules (Kaviani, 1995), producing a very complex, but efficient, heat transfer interface in an ionanofluid.

The heat capacity data of these cherry stones and other fruit seeds (natural micro and nanomaterials), shells and pits, are shown, as a function of temperature, in Figure 12. These include walnut and hazelnut shells, annona (custard apple) fruit seeds, peach pits and olive stones (Queirós, 2010). The plot shows that the heat capacity of all samples increases up to a maximum between 350 and 370 K, decreasing then to very small values (around 1 $Jg^{-1}K^{-1}$).

Remembering that the heat capacity of liquid water is around $4 \text{ Jg}^{-1}\text{K}^{-1}$, it can be seen that the maximum values can be as great as $10 \text{ Jg}^{-1}\text{K}^{-1}$ (walnut shell) or $9.4 \text{ Jg}^{-1}\text{K}^{-1}$ (cherry stone), the lowest value being obtained for the olive stone ($4.3 \text{ Jg}^{-1}\text{K}^{-1}$). The shape of the curves is the

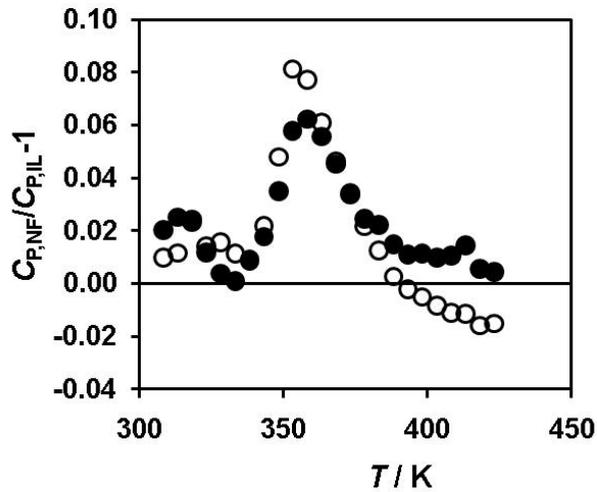


Fig. 10. Heat capacity enhancement of $[\text{C}_4\text{mim}][\text{PF}_6]$ -based ionanofluid for two different MWCNTs loadings as a function of temperature (legends: \square - $[\text{C}_4\text{mim}][\text{PF}_6]$ + 1 wt% MWCNTs; \circ - $[\text{C}_4\text{mim}][\text{PF}_6]$ + 1.5 wt% MWCNTs)

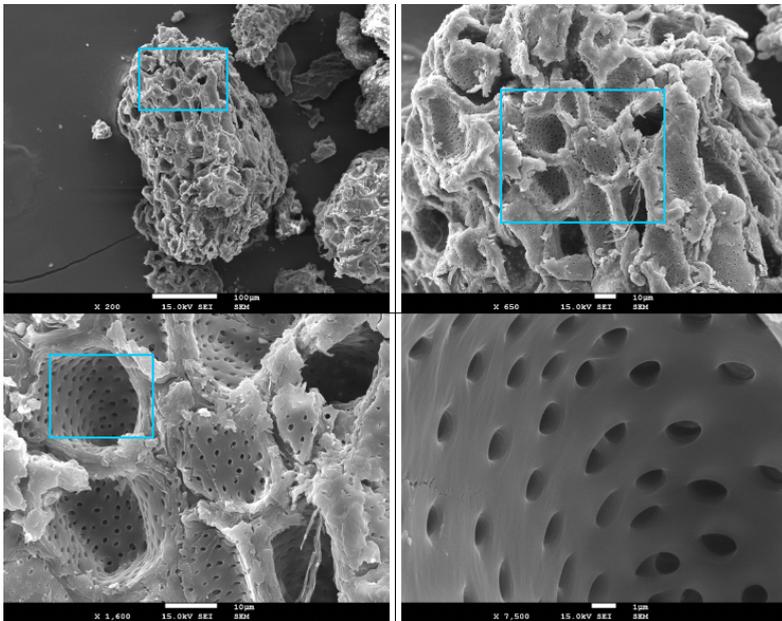


Fig. 11. FEG-SEM images of cherry stones bits for different magnifications (Queirós, 2010).

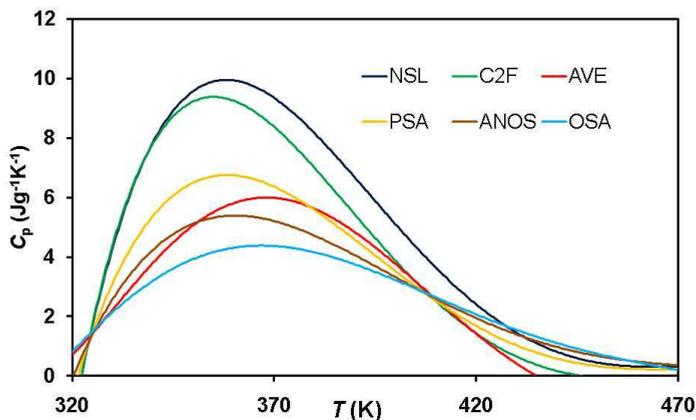


Fig. 12. Temperature-dependent heat capacity of several fruit seeds (legend: NSL – walnut shell; AVE – hazelnut shell; C2F – cherry stones; ANOS – annona fruit seed; PSA – peach pit; OSA – olive stone).

same, and the change in the temperature of the maximum is very small (10 K), facts that seem to demonstrate that the structure of these materials is similar, although the absolute capacity to store heat changes from material to material. Keeping in mind that the densities of these materials vary between 0.7 and 1.1 gcm⁻³, the heat storage density or the heat capacity per unit volume (ρC_p) can vary between 2.9 and 11 Jcm⁻³K⁻¹, a factor of 2 to 6 greater than common heat transfer oils and 1.5 to 5.5 greater than ionic liquids (França et al, 2009). These values suggest that ionanofluids based on these nanomaterials are excellent heat storage and transfer fluids and that ionanofluids can replace the existing aliphatic, aromatic and silicone oils used in the industry, as biodegradable, non-toxic and more efficient in terms of heat transfer load and capacity, namely for microchannel heat exchangers.

6. Conclusions

In this chapter, thermal conductivity and heat capacity of several ionic liquids and MWCNTs-ionanofluids as a function of temperature are presented and analyzed. The thermal conductivity data obtained have an uncertainty of 3-5% and, where available, are in good agreement with the available reported data. Present data for the heat capacity of ionic liquids also agree well with published data and have an estimated uncertainty of 1%. In the case of ionanofluids, the data are completely new and cannot be compared with other data. Moderate enhancements of thermal conductivity (between 2 and 9%) were observed for the ionanofluids in comparison with the base ionic liquids and the thermal conductivity showed a weak dependence on temperature.

Present results on specific heat capacity of ionic liquids agree well with the best values obtained with adiabatic calorimetry and DSC measurements from literature. For heat capacity of ionanofluids, an enhancement of up to 8% was found for C₄mim][PF₆] with both 1 wt% and 1.5 wt% of MWCNTs, a phenomena found for the first time for nanofluids.

The behavior of these ionanofluids together with the specific behavior of ionic liquids studied suggest the existence of nanocluster formation and preferred paths for heat transfer and storage, a fact that will be the subject of further studies.

The mass production of ionic liquids has not yet been attained; however, when it should, we would be able to replace actual non-biodegradable and environmental harmful heat transfer fluids. In addition, due to their increased heat storage capacity as compared with traditional heat transfer fluids, they have the potential to use in shell and tube heat exchangers, and in other small capacity heat exchangers like micro-channels.

In addition, the use of natural and therefore recyclable and biodegradable nanomaterials, that can replace the CNT's, can provide a great change in the field, due to its big heat capacity, as shown with the results presented for fruit seeds.

With the fascinating features of ionanofluids such as high thermal conductivity, high heat storage capacity and non-volatile nature, they can potentially be used as novel heat transfer fluids. Nonetheless, besides studying thermal conductivity measurement, more experimental and theoretical investigations on heat capacity and viscosity of ionanofluids are imperative in order to exploit their potential applications in numerous important fields.

7. Acknowledgments

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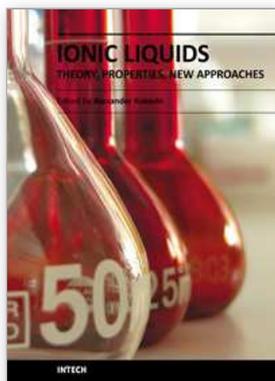
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Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

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