Chapter 8
Ionanofluids: New Heat Transfer Fluids for Green Processes Development

Carlos A. Nieto de Castro, S.M. Sohel Murshed, Maria J.V. Lourenço, Fernando J.V. Santos, Manuel L.M. Lopes, and João M.P. França

Abstract Ionanofluids represent a new and innovative class of heat transfer fluids that encompass multiple disciplines like nanoscience, mechanical, and chemical engineering. Apart from fascinating thermophysical properties, the most compelling feature of ionanofluids is that they are designable and fine-tunable through base ionic liquids. Besides presenting results on thermal conductivity and specific heat capacity of ionanofluids as a function of temperature and concentration of multiwall carbon nanotubes, findings from a feasibility study of using ionanofluids as replacement of current silicon-based heat transfer fluids in heat transfer devices such as heat exchangers are also reported. By comparing results on thermophysical properties and estimating heat transfer areas for both ionanofluids and ionic liquids in a model shell and tube heat exchanger, it is found that ionanofluids possess superior thermophysical properties particularly thermal conductivity and heat capacity and require considerably less heat transfer areas as compared to those of their base ionic liquids. This chapter is dedicated to introducing, analyzing, and discussing ionanofluids together with their thermophysical properties for their potential applications as heat transfer fluids. Analyzing present results and other findings from pioneering researches, it is found that ionanofluids show great promises to be used as innovative heat transfer fluids and novel media for the exploitation of green energy technologies.

C.A. Nieto de Castro (✉) • S.M.S. Murshed • M.J.V. Lourenço • F.J.V. Santos • M.L.M. Lopes • J.M.P. França
Centre for Molecular Sciences and Materials, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Lisbon, Campo Grande, Lisbon 1749-016, Portugal
e-mail: cacastro@fc.ul.pt; smmurshed@fc.ul.pt; mjvl@fc.ul.pt; fjsantos@fc.ul.pt; mllopes@fc.ul.pt

A. Mohammad and Inamuddin (eds.), *Green Solvents I: Properties and Applications in Chemistry*, DOI 10.1007/978-94-007-1712-1_8,

8.1 Introduction

The concept of "ionanofluids" was recently coined by Nieto de Castro and coworkers [1], and it represents a very new class of heat transfer fluids where nanoparticles are dispersed in ionic liquids only [2]. Since ionanofluids are a specific type of nanofluids, that is, ionic liquid-based nanofluids, it is important to provide background of nanofluids before discussing development and potential applications of ionanofluids in this section.

8.1.1 Nanofluids

Many high-tech industries and thermal management systems are facing great technical challenges for cooling of smaller features of microelectronic and more power output-based devices. However, the conventional method to increase the cooling rate is to use extended heat transfer surfaces, but this approach requires an undesirable increase in the size of the thermal management systems. In addition, the inherently poor thermal properties of traditionally used heat transfer fluids (HTFs) such as water, ethylene glycol (EG), or engine oil (EO) greatly limit the cooling performance. Thus, these conventional cooling techniques are not suitable to meet the cooling demand of the high-tech industries and advanced devices. It is known that fluids possess order-of-magnitude smaller thermal conductivity than metallic or nonmetallic materials. Therefore, the thermal conductivities of fluids that contain suspended metallic or nonmetallic particles are expected to be significantly higher than those of traditional heat transfer fluids.

It was only in 1995 that Choi [3] at Argonne National Laboratory of USA coined the concept of "nanofluids" to meet the aforementioned cooling challenges facing many advanced industries and devices. This new class of heat transfer fluids (nanofluids) is engineered by dispersing nanometer-sized solid particles, rods, or tubes in traditional heat transfer fluids, and they were found to exhibit significantly higher thermophysical properties, particularly thermal conductivity and thermal diffusivity than those of base fluids (BFs) [4–9]. From practical application-based studies such as convective and boiling heat transfer characteristics [10–16], nanofluids (NFs) were also found to be even more promising as their convective heat transfer coefficient and critical heat flux were reported to be substantially higher as compared to those of their base fluids. In particular, nanofluids containing high thermal conductive materials such as carbon nanotubes (CNT) show anomalously enhanced thermal performance [16–18]. Thus, nanofluids have attracted great interest from the research community due to their enhanced thermophysical properties, potential benefits, and applications in numerous important fields. Recent record shows that there is an exponential growth of annual research publications on nanofluids, and there are also more than 300 research groups and companies worldwide who are involved with nanofluids research [19].

The impact of nanofluid technology is expected to be great considering that heat transfer performance of heat exchangers or cooling devices is vital in numerous industries. When the nanoparticles are properly dispersed, nanofluids can offer numerous benefits besides their anomalously high effective thermal conductivity. The benefits include improved heat transfer and thermal stability, microchannel cooling without clogging, miniaturized systems, and reduction in pumping power. With these highly desirable thermal characteristics and potential benefits, nanofluids can have a wide range of applications such as microelectronics, microelectromechanical systems, microfluidics, transportation, manufacturing, instrumentation, medical, and heating-ventilating-air-conditioning systems [8].

8.1.2 Ionanofluids and Their Prospect as Heat Transfer Fluids

The term *ionanofluids* is defined as the suspensions of nanomaterials (particles, tubes, and rods) in ionic liquids [1, 2, 20], and it is a new term in multidisciplinary fields such as nanoscience, nanotechnology, thermofluid, chemical, and mechanical engineering. Since ionic liquids (ILs) are the base fluids in ionanofluids, their thermophysical properties, potential benefits, and applications will also be discussed in short.

In the past decades, significant progress has been made toward better understanding and practical application of ionic liquids. Extensive research efforts [21–30] have been devoted to ionic liquids which have proven to be safe and sustainable alternatives for many applications in industry and chemical manufacturing. Their prospect and success arise mainly from their thermophysical and phase-equilibria properties, the versatility of their synthesis, and manageability to be tailored for a given application. Their solvent properties as well as heat transfer or heat storage and surface properties make this class of fluids possible to use in a high plethora of applications [25, 31]. Other advantages of ionic liquids include high ion conductivity, high volumetric heat capacity, high chemical and thermal stabilities, negligible vapor pressure, wide range of viscosity, and very good solvent properties [22, 24, 29, 30]. Due to all of these fascinating characteristics, they have been investigated extensively as alternatives to molecular solvents for liquid-phase reactions [27]. Ionic liquids are of great interest to scientists as well as chemical companies, not only because of their remarkable properties, but also for their actual and potential applications in the chemical process industries. In the past, the values of their thermophysical properties were found to have significant effect on the design of physicochemical processing and reaction units by influencing directly the design parameters and performance of equipments like heat exchangers, distillation columns, and reactors [32]. However, the optimal technological design of green processes requires the characterization of the ionic liquids used, namely, their thermodynamic, transport, and dielectric properties. Recently, our group has reported studies [1, 2, 31–34] where measured data on various thermophysical properties of a wide range of ionic liquids are presented besides studying their potential application as heat transfer fluids as well as their properties measurement methods and uncertainties. Results from these studies indicate that ionic liquids possess promising thermophysical properties and great potential for numerous applications, particularly as new heat transfer fluids.

The discovery that carbon nanotubes and room-temperature ionic liquids can be blended to form gels termed as "bucky gels" which can potentially be used in many engineering or chemical processing such as making novel electronic devices, coating materials, and antistatic materials, and, thus, it opens a completely new field [35, 36]. The "bucky gels" are blends or emulsions of ionic liquids with nanomaterials, mostly nanocarbons (tubes, fullerenes, and spheres), and they are actually CNT-laden ionanofluids. The possibility of using ionic liquids containing dispersed nanoparticles with specific functionalization such as functionalized single-walled carbon nanotubes (SWCNT), multiwalled carbon nanotubes (MWCNT), and fullerenes (C60, C80, etc.) opens the door to many applications. The use of nanoparticles as heat transfer enhancers allows us to associate small quantities of different types of nanomaterials to ionic liquids to prepare 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 task. This is possibly due to the complex interactions of ionic liquids and nanomaterials in the created complex emulsions. In contrast to conventional nanofluids, ionanofluids are more flexible as their base fluids are ionic liquids which can be prepared or designed for specific properties as well as for specific tasks.

Recent studies performed by this group (Nieto de Castro and coworkers) showed that ionanofluids containing MWCNT exhibit enhanced thermal conductivity (ranging from 2% to 35%) and specific heat capacity compared to their base ionic liquids [1, 2]. Since these ionanofluids have fascinating features such as high thermal conductivity, high volumetric heat capacity, and nonvolatility, they can potentially be used as novel heat transfer fluids. Another important application of ionanofluids is that they can be used in the development of new pigments for paint coatings of solar collectors with their higher solar absorbance and thermal emissivity as compared to the base paint [37]. Except researches conducted by this group, no other work on ionanofluids is available in the literature.

This chapter deals with the temperature and concentration dependence of thermal conductivity and specific heat capacity of ionanofluids containing MWCNT in several ionic liquids. Results of the thermal conductivity of these ionanofluids are also compared with the thermal conductivity data for MWCNT-nanofluids obtained from the literature. With the remarkable thermophysical properties and great flexibility of designing of ionanofluids for specific tasks and for particular properties, it can plausibly be considered that along with numerous applications, this new class of heat transfer fluids can potentially be used for the development of green processes.

8.2 Preparation of Ionanofluids

As mentioned previously, ionic liquids have been considered as potential heat transfer fluids not only due to their high volumetric heat capacity and good thermal conductivity (similar to conventional HTFs such as Dowtherm MX™, Syltherm 800™, and engine oil) but also for their high thermal stability and low vapor pressure.

Table 8.1 Reference values of thermophysical properties of some commonly used heat transfer fluids and ionic liquids at a moderate temperature of 40°C

Liquids	λ (W/m·K)	η (mPa·s)	C_p (J/kg·K)	ρ (kg/m^3)
Water	0.631	0.653	4,179	992
Ethylene glycol	0.256	10.37	2,520	1,100
Engine oil	0.148	568.00	2,000	880
[C_4mim][NTf_2]	0.116	28.50	1,372	1,423
[C_2mim][$EtSO_4$]	0.178	50.00	1,615	1,226

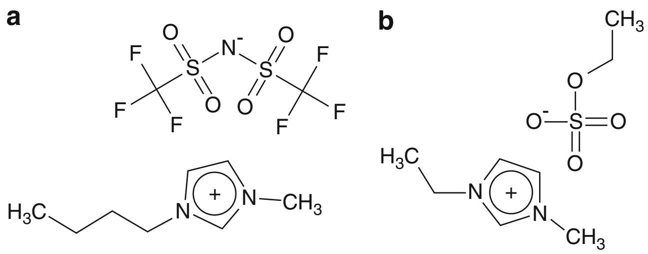

Fig. 8.1 Structures of ionic liquids (**a**) [C_4mim][NTf_2] and (**b**) [C_2mim][$EtSO_4$]

Reference values of thermophysical properties of some commonly used heat transfer fluids and ionic liquids used to prepare ionanofluids at a moderate temperature (40°C) are provided in Table 8.1 [38, 39]. Ionic liquids used were synthesized and purified following the procedure given elsewhere [40]. They were prepared through metathesis reactions from the appropriate [$C_n$mim]Cl. Prior to use, samples were extensively washed with distilled water and dried while stirring overnight at 70°C under high vacuum (0.1 Pa). Sample ionic liquids were analyzed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and elemental analysis. The water content was measured using Karl Fischer titration before and after each measurement. The ionic liquids used were 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl} imide ([C_4mim][NTf_2]), 1-butyl-3-methylimidazoliuethylsulfate ([C_4mim][$EtSO_4$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4], and 1-hexyl-3-methylimidazolium tetrafluoroborate [C_6mim][BF_4]). Structures of two representative ionic liquids (i.e., [C_4mim][NTf_2] and [C_2mim][$EtSO_4$]) are shown in Fig. 8.1.

Multiwalled carbon nanotubes (Baytubes®), provided by Bayer Material Science (Germany), were produced from a high-yielding catalytic process based on chemical vapor deposition. Baytubes® are agglomerates of multiwall carbon nanotubes with small outer diameters, narrow diameter distribution, and ultrahigh aspect ratio (length-to-diameter ratio). According to Bayer Material Science, the purity of MWCNT purchased was >99%, and the outer mean diameter and length of nanotubes were 13–16 nm and 1–10 μm, respectively. Following the technique used by Aida and coworkers [35, 36], sample ionanofluids were prepared by dispersing different weight percentages of MWCNT in several ionic liquids, and they were sonicated for better dispersion of nanotubes. All MWCNT suspensions were found

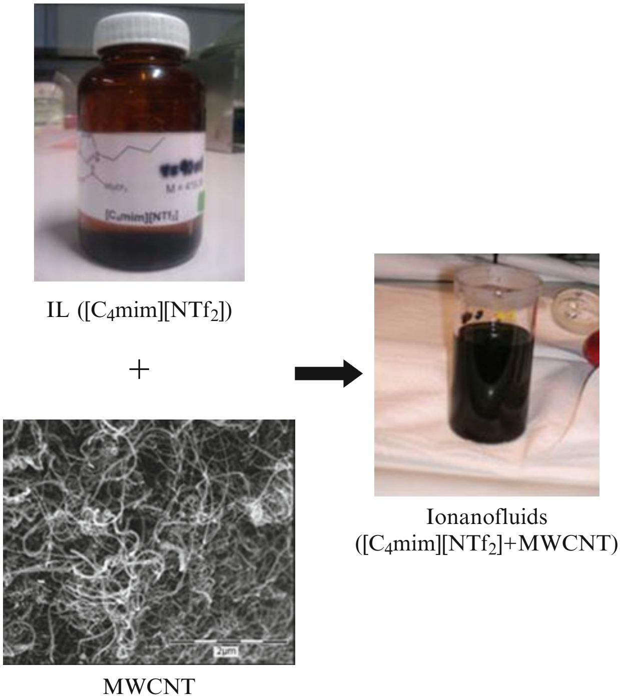

Fig. 8.2 Picture of MWCNT/[C_4mim][NTf_2]-based ionanofluids

to be very stable. A representative pictures of a sample ionanofluid containing MWCNT in [C_4mim][NTf_2] ionic liquid is shown in Fig. 8.2. The color of this ionanofluid is black due to dispersed carbon nanotubes.

8.3 Experimental and Measurement Details

The thermal conductivity of sample fluids was measured using a KD2 Pro Thermal Properties Analyzer (Labcell Ltd., UK). The theoretical basis and measurement principle of KD2 are basically the same as the transient hot-wire technique. The KD2 Pro is a handheld device used to measure thermal properties. It consists of a controller and sensors (probes) that can be inserted into the sample medium whose thermal properties are to be measured. There are three probes: the standard single-needle probe, an extended-length single-needle probe, and a dual-needle probe. While the single-needle probe measures the thermal conductivity and resistivity, the dual-needle probe is used to measure the thermal diffusivity and volumetric specific heat capacity.

As the ionic liquids are electrically conducting liquids, an electrically isolated thermal probe coated with a thin coating of an insulator is used. Thermal probe of this KD2 analyzer contains both the heating element and thermoresistor, and it needs to be inserted into the sample vertically, rather than horizontally, in order to minimize the possibility of inducing convection. The measurement is made by electrically heating the probe within the sample while simultaneously monitoring the temperature change of the probe. A microprocessor or controller connected to the probe is used to control the heating rate and to measure the temperature change data. Details about KD2 Pro can be found in its user manual. A parameter-corrected version of the temperature model developed by Carslaw and Jaeger [41] for an infinite line heat source with constant heat output and zero mass in an infinite medium is used to calculate the thermal conductivity.

Before measuring the thermal conductivity of sample liquids, the KD2 Pro was carefully calibrated using toluene, water, glycerol, mixture of glycerol and water, and aqueous sodium chloride solution in order to cover the range of thermal conductivities between 0.13 and 0.67 W/m K. The calibration constant was found to be 1.026 ± 0.034, and it was temperature-independent [39]. Small quantity of sample to be analyzed was then 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 immersed in a thermostatic bath (Haake C25) which allowed controlling and maintaining the temperature of the test sample at any desired value. Several measurements were taken at each temperature to ensure reproducibility of the measured data, and the average values are reported. More details about the measurement procedure can be found in a work [42] where KD2 Pro device was also used for measuring thermal conductivity of several ionic liquids. Based on the standard deviations of experimental and calibration data, the uncertainty of the thermal conductivity measurements was found to be in the range of ±0.008 to ±0.014 W/m·K.

A calibrated differential scanning calorimeter (DSC-111, Setaram, France) was used to measure the specific heat capacity of sample fluids. The operation of this DSC is based on the Tian-Calvet principle, and it uses a cylinder-type measuring system composed of 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 [43, 44].

8.4 Results and Discussion

8.4.1 Thermal Conductivity of Ionanofluids

Results on temperature and concentration dependence of thermal conductivity of several MWCNT-ionanofluids obtained by our group together with the data of CNT/water-based nanofluids from the literature are presented and discussed in this section. Since a lot of research efforts [17, 18, 45, 46] have been made on the thermal conductivity of CNT-nanofluids, comparison of results of CNT-nanofluids and

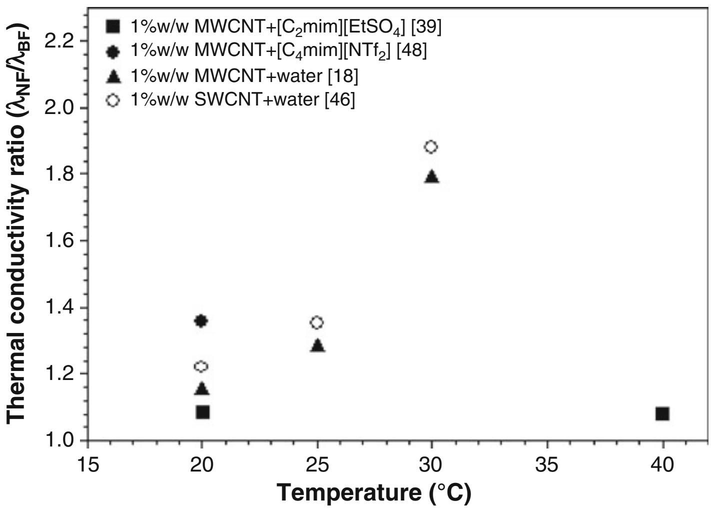

Fig. 8.3 Effect of temperature on thermal conductivity of CNT-loaded nanofluids and ionanofluids

CNT-ionanofluids can provide quantitative information about the enhancement of thermal conductivity of these two innovative heat transfer fluids. Most of the previous studies with CNT-nanofluids showed substantial increase in thermal conductivity compared to their base fluids. For instance, for 1% volumetric loading of MWCNT, Choi et al. [17] found as high as 160% increase in thermal conductivity of α-olefin oil ($\lambda = 0.145$ W/m·K), and Xie et al. [45] reported about 13% and 19.6% increases in thermal conductivity of ethylene glycol ($\lambda = 0.256$ W/m·K) and decene ($\lambda = 0.14$ W/m·K), respectively. Besides understanding the potential of ionanofluids as novel heat transfer fluids, any comparison of enhancements of thermal conductivity of ionanofluids and nanofluids will make it easy to understand the comparative advantages of ionic liquids as base fluids that can be designed for specific tasks and properties oriented. Since no data are available in the literature for temperature-dependent thermal conductivity of ionanofluids, no comparison of present results can be made.

Temperature-dependent thermal conductivity of ionanofluids containing 1 wt% of MWCNT in [C_4mim][NTf_2] and [C_2mim][$EtSO_4$] and nanofluids containing the same concentrations of MWCNT and SWCNT in water are presented in Fig. 8.3. It can be seen from Fig. 8.3 that at room temperature, [C_4mim][NTf_2]-based ionanofluid showed maximum 35.5% increase in thermal conductivity compared to its base ionic liquid, whereas [C_2mim][$EtSO_4$]-based ionanofluid showed only 8.5% increase in thermal conductivity over its base fluids, and no temperature dependence of this thermal conductivity is observed. On the other hand, at the same temperature and concentration, thermal conductivity data of MWCNT/water-based nanofluids reported by Ding et al. [18] and data of SWCNT/water-based nanofluids obtained from Amrollahi et al. [46] showed about 15% and 22% increases in thermal

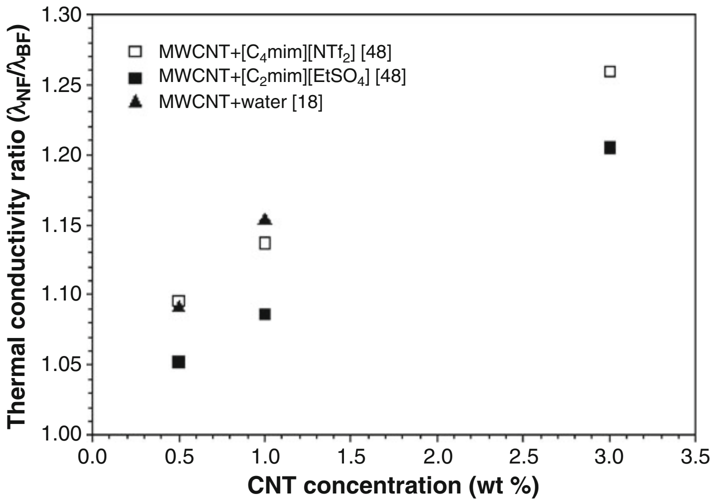

Fig. 8.4 Thermal conductivity enhancement of nanofluids and ionanofluids as a function of concentration of MWCNT at room temperature

conductivity, respectively (Fig. 8.3). It is also noted that for better dispersion and stability of nanofluids, Ding et al. [18] used 0.25 wt% Gum Arabic stabilizer with their nanofluids, and Amrollahi et al. [46] added 1 wt% SDS surfactant to their SWCNT nanofluids. Thus, it can be demonstrated that at room temperature, [C_4mim][NTf_2]-based ionanofluids is much better conductive suspensions than aqueous CNT-nanofluids. Figure 8.3 also shows that while the thermal conductivity of these CNT-nanofluids increase substantially with increasing temperature, the thermal conductivity of the reported ionanofluid is found to be independent of temperature. The reasons for such temperature-independent nature of ionanofluids are not well understood at this moment. However, similar temperature independence of thermal conductivity of nanofluids was reported in the literature. For example, Venerus et al. [47] found that level of thermal conductivity enhancement for Al_2O_3/petroleum oil-based nanofluid is independent of temperature in the range of 27–77°C. In fact, they observed a slight decrease in thermal conductivity of Au/water-based nanofluids with the increasing temperature. Figure 8.4 demonstrates that thermal conductivity enhancement of two ionanofluids and one nanofluid is a function of concentration of MWCNT at room temperature. It is seen that the thermal conductivity of ionanofluids (λ_{INF}) increases significantly (almost linear) over base ionic liquid with weight concentration of MWCNT.

Effects of temperature and MWCNT concentration on thermal conductivity of [C_2mim][$EtSO_4$]-based ionanofluids are shown in Fig. 8.5. Maximum enhancement of thermal conductivity of 25% is observed at 71°C and at 3 wt% concentration of MWCNT in this ionic liquid. It is also seen that the higher the concentration of MWCNT, the larger is the enhancement in thermal conductivity. However, the effect of temperature on the enhancement of thermal conductivity is not significant, and

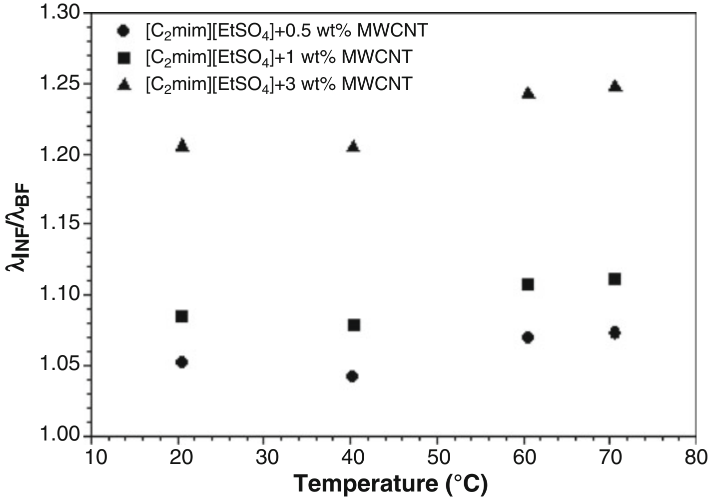

Fig. 8.5 Effect of temperature and MWCNT concentration on thermal conductivity enhancement of $[C_2mim][EtSO_4]$-based ionanofluids [39]

Table 8.2 Experimental data of thermal conductivity of various ionic liquids and their ionanofluids with 1 wt% of MWCNT at room temperature [48]

Ionic liquids	λ_{IL} (W/m·K)	Ionanofluids	λ_{INF} (W/m·K)	Increase of λ_{INF} (%)
$[C_2mim][NTf_2]$	0.123	$[C_2mim][NTf_2]$/MWCNT	0.126	2.44
$[C_4mim][NTf_2]$	0.121	$[C_4mim][NTf_2]$/MWCNT	0.164	35.54
$[C_4mim][CF_3SO_3]$	0.142	$[C_4mim][CF_3SO_3]$/MWCNT	0.155	9.44
$[C_6mim][NTf_2]$	0.122	$[C_6mim][NTf_2]$/MWCNT	0.130	6.81
$[C_8mim][NTf_2]$	0.121	$[C_8mim][NTf_2]$/MWCNT	0.129	6.62
$[C_4mim][BF_4]$	0.163	$[C_4mim][BF_4]$/MWCNT	0.173	6.13
$[C_6mim][BF_4]$	0.157	$[C_6mim][BF_4]$/MWCNT	0.163	4.01

these ionanofluids are found to be more stable at higher temperature (>60°C) and concentration of MWCNT. This might be because the layer structure built for this ionanofluid is more stable when subjected to a higher temperature. It is however interesting to note that changes in thermal conductivity of this ionanofluids with respect to temperature are not significant, and at some higher temperatures, the thermal conductivity values were found to be smaller than those at lower temperature. For pure ionic liquids, similar temperature-independent nature of thermal conductivity was also previously reported [2]. This indicates that there might be no or weak temperature-related mechanism for the enhancement of the thermal conductivity of these ionanofluids.

Results of thermal conductivity of several other MWCNT-ionanofluids and their base ionic liquids at room temperature are presented in Table 8.2. Except $[C_4mim]$

$[NTf_2]$-based ionanofluids, most of other ionanofluids show low or moderate increase in thermal conductivity at 1 wt% concentration MWCNT. Therefore, it is clear that not all ionic liquids can give high thermal conductivity when CNT (or other nanoparticles) are dispersed in them. The CNT when dispersed in the ionic liquid are likely to interact preferentially with the nonpolar domains associated with the alkyl chains, thus creating microclusters that can enhance the heat transfer. The procedure for the ionanofluids preparation is also crucial for the value of the enhancement, as discussed in [39], as the structure of the emulsion is fundamental.

8.4.2 Specific Heat Capacity of Ionanofluids

Besides thermal conductivity, specific heat capacity of ionanofluids is of great importance for their practical applications in thermal system management and green energy–based areas. Knowledge of this important property is also essential in determining other heat transfer properties, flow features, as well as enthalpy calculations in various processes simulation.

The potential use of ionic liquids as heat transfer fluids particularly in heat exchanger in chemical plants and solar thermal power generation (from cryogenic temperatures up to 200°C) depends on the values of volumetric heat capacity, vapor pressures, and thermal stability which have previously been discussed [26]. Comparison of properties of ionic liquids with synthetic compounds (based on hydrocarbons, polyaromatics, and siloxanes) showed that common imidazolium systems have higher heat capacities per unit volume than the reported commercial thermal fluids such as Paratherm HE® and Dowtherm MX™ [32].

Figure 8.6 illustrates that volumetric heat capacities of various ionic liquids such as 1-ethyl-3-methylimidazolium hexafluorophosphate ($[C_2mim][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$), 1-ethyl-3-methylimidazolium tetrafluoroborate ($[C_2mim][BF_4]$), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4mim][CF_3SO_3]$), and 1-butyl-3-methylimidazoliumoctylsulfate ($[C_4mim][C_8H_{17}SO_4]$) as well as high-performance commercial heat transfer fluids (Dowtherm MX™ and Paratherm HE®) increase significantly and linearly with increasing temperature. These data are obtained from material safety data sheets and ILThermo database of National Institute of Standards and Technology, Colorado, USA. It is noted that Dowtherm MX™ is a mixture of alkylated aromatics, while Paratherm HE® is a paraffinic hydrocarbon. Similar increase in specific heat capacities of various ionic liquids with respect to temperature is also reported by Ge et al. [49]. It can be seen from Fig. 8.6 that the volumetric heat capacity of ionic liquids are higher than these commercial heat transfer fluids. It is, therefore, anticipated that the specific heat capacity of ionanofluids will also increase with temperature. Figure 8.7 depicts that the specific heat capacity of MWCNT-ionanofluids increases significantly with increasing temperature compared to its base ionic liquid, $[C_4mim][PF_6]$. The most interesting part of these results is that regardless of MWCNT loading, there was dome-shaped jump of the specific heat capacity enhancement

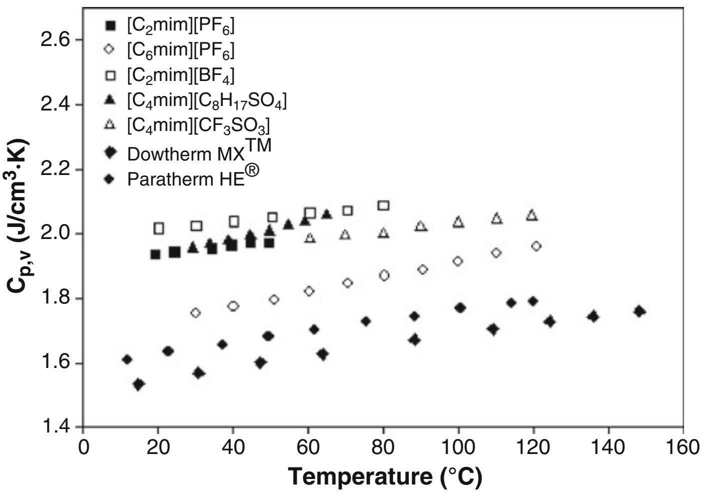

Fig. 8.6 Effect of temperature on volumetric heat capacity of several ionic liquids and heat transfer fluids

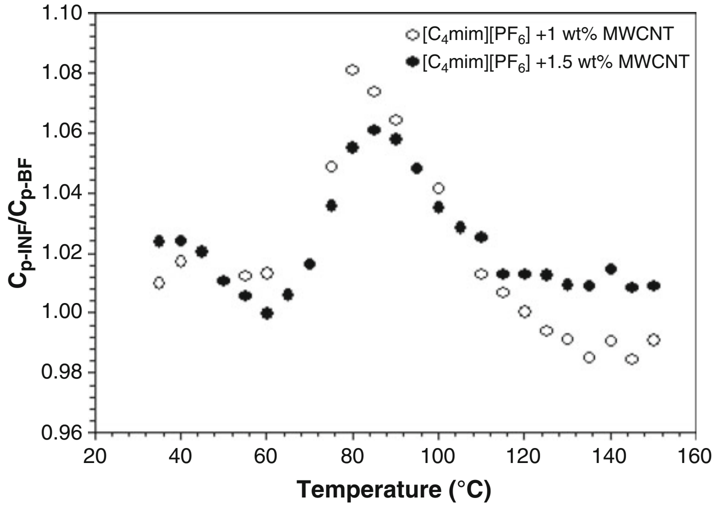

Fig. 8.7 Effect of temperature on heat capacity of ionanofluids at two different concentrations of MWCNT [2]

(a peak increase of 8% compared with base IL) at a certain temperature range (60–110°C). The reasons for such mysterious results are not well understood at this stage. There was little increase in specific heat capacity of ionanofluids with increasing loading of MWCNT. Nevertheless, any increase in heat capacity of any fluids is of great importance for their practical applications as heat transfer fluids.

Table 8.3 Values of thermophysical properties of ILs and HTFs and estimated reference heat transfer area (A_0) for the shell and tube heat exchanger [32]

ILs and HTFs	ρ (kg/m^3)	C_p (J/kg·K)	η (mPa·s)	λ·(mW/m·K)	A_0 (m^2)
[C_4mim][PF_6] (50°C)	1,346 ± 1	1,493 ± 30	68.8 ± 1.8	146 ± 7	480.75
[C_6mim][PF_6] (50°C)	1,273 ± 3	1,409 ± 61	111.9 ± 3.2	146 ± 7	634.60
[C_2mim][BF_4] (50°C)	1,280 ± 2	1,600 ± 25	15.9 ± 1.1	196 ± 6	217.29
Dowtherm A™ (50°C)	1,041	1,632	2.12	134	138.60
Dowtherm MX™ (100°C)	905	1,870	2.09	114	159.08
Syltherm 800™ (80°C)	882	1,711	3.86	124	202.86

8.4.3 Comparisons of Thermophysical Properties and Heat Transfer Areas

The values of thermophysical properties of liquids have a significant effect on the design of physicochemical processing, reaction units, and heat transfer devices, as they influence directly the design parameters and performance of equipments like heat exchangers, distillation columns, and reactors [50, 51]. Our group previously analyzed the same effect for molten alkali nitrates [52], which have emerged as high-temperature fluids for several technological processes such as high-temperature energy storage in batteries for solar plants and waste treatment. It was demonstrated that the knowledge of accurate data for the transport coefficients of these fluids is very important.

Ionic liquids are presently a good challenge to both scientists and chemical companies for their actual and potential applications in the chemical process industries and thermal management systems. Recently, our group studied the possibility of using ionic fluids as replacement of current silicon-based heat transfer fluids in heat transfer devices and made comparisons of heat storage capacity, other thermophysical properties, and heat transfer areas with current heat transfer fluids [32]. Details of the simulation, operation conditions, and cost estimation of a model shell and tube heat exchanger can be found elsewhere [32]. The values of the thermophysical properties of several heat transfer fluids (Dowtherm Co.) and ionic liquids used together with the calculated values of reference heat transfer area (A_0) for each heat transfer fluids and ILs are provided in Table 8.3. It can be demonstrated (Table 8.3) that although the heat capacity per unit volume of ionic liquids is significantly larger (20–50%) compared to these heat transfer liquids, the heat transfer areas may be comparable or bigger, which raises the cost of such equipment. For other ionic liquids, similar results are anticipated. It is also known that the influence of actual errors in the thermophysical properties of ionic liquids can render any future design as not working or excessively costing [32].

Very recently, França [39] performed simulation to estimate reference heat transfer area using two ionic liquids, ([C_4mim][NTf_2] and [C_2mim][$EtSO_4$]), as well as their ionanofluids containing 1 wt% of MWCNT under the same flow and other parameters in the same shell and tube heat exchanger used in previous study [32].

Table 8.4 Values of thermophysical properties and reference area A_0 for the shell and tube heat exchanger using $[C_4mim][NTf_2]$ and $[C_2mim][EtSO_4]$ ionic liquids and their MWCNT ionanofluids at 40°C

ILs and INFs	λ (W/m·K)	η (mPa·s)	C_p (J/kg·K)	ρ (kg/m^3)	A_0 (m^2)
$[C_4mim][NTf_2]$	0.1164	28.50	1,372.44	1,422.99	364.627
$[C_4mim][NTf_2]$ + 1 wt% MWCNT	0.1290	31.58	1,396.03	1,422.99	355.537
$[C_2mim][EtSO_4]$	0.1751	50.01	1,614.96	1,226.10	383.892
$[C_2mim][EtSO_4]$ + 1 wt% MWCNT	0.1890	53.98	1,642.72	1,226.06	376.130

Thermophysical properties and simulated heat transfer areas for these ionic liquids and ionanofluids are shown in Table 8.4. It can be seen that there is maximum 2.5% decrease in reference heat transfer area (A_0) due to the addition of 1 wt% of MWCNT in the base IL. This indicates that ionanofluids will perform better than ionic liquids in heat transfer devices like heat exchangers. Based on the high convective heat transfer performance of conventional nanofluids [8, 14, 15, 18], it is plausible to believe that using nanofluids, the heat transfer area can be reduced considerably compared to their base heat transfer fluids. França [39] also performed simulation for estimation of the total cost for model shell and tube heat exchanger operating with these ionic liquids as well as ionanofluids and showed that such reduction (2.5%) in heat transfer area could reduce the total cost by 1.7%.

8.5 Conclusions

This chapter presents preliminary overview of various aspects of ionanofluids as well as experimental findings on their thermophysical properties. Background of development of ionanofluids together with brief review on pioneering research works performed by the authors of this chapter and other groups is provided. Since ionanofluids are ionic liquid-based nanofluids, details about nanofluids and ionic liquids are also discussed. Besides presenting results on two major thermophysical properties (thermal conductivity and specific heat capacity) of MWCNT-ionanofluids as a function of temperature and concentration, a model feasibility study of using ionanofluids as replacement of current silicon-based heat transfer fluids in heat exchangers is also reported. Comparisons of available data of various thermophysical properties of commercial heat transfer fluids, ionic liquids, and ionanofluids are made in order to have better knowledge and quantitative information on the increase or decrease of these properties of ionanofluids as compared to other fluids.

It is found that ionanofluids show great promises to be used as innovative heat transfer fluids and novel media for many green energy–based applications. The values of thermophysical properties of liquids have a significant effect on the design and development of green processes and heat transfer devices. Results show that ionanofluids exhibit superior thermophysical properties compared to base ionic liquids, and simulated results on heat transfer areas from a model study indicate a decrease in reference heat transfer area of a shell and tube heat exchanger due to addition of 1 wt% of MWCNT in base ionic liquid. This indicates that ionanofluids are better heat transfer fluids for heat exchangers or other heat transfer devices than ionic liquids.

Besides their heat transfer–based applications in green processes design and developments, ionanofluids have many more uncovered potential applications in various important fields. As an innovative class of fluids, there are plenty of possibilities open to this new area of ionic liquids as heat transfer fluids and more developments in ionanofluids are expected to be seen in the future.

Acknowledgment The authors would like to thank FCT-Fundação para a Ciência e Tecnologia, Portugal, for financial support under grant PTDC/EQU-FTT/104614/2008 for this work.

References

1. Ribeiro APC, Lourenço MJV, Nieto de Castro CA (2009) Thermal conductivity of ionanofluids. In: 17th symposium on thermophysical properties, Boulder, USA, 2009
2. Nieto de Castro CA, Lourenço MJV, Ribeiro APC, Langa E, Vieira SIC, Goodrich P, Hardacre C (2010) Thermal properties of ionic liquids and ionanofluids of imidazolium and pyrrolidinium liquids. J Chem Eng Data 55:653–661
3. Choi SUS (1995) Enhancing thermal conductivity of fluids with nanoparticles. ASME FED 231:99–105
4. Lee S, Choi SUS, Li S, Eastman JA (1999) Measuring thermal conductivity of fluids containing oxide nanoparticles. J Heat Transf 121:280–289
5. Murshed SMS, Leong KC, Yang C (2005) Enhanced thermal conductivity of TiO_2-water based nanofluids. Int J Therm Sci 44:367–373
6. Murshed SMS, Leong KC, Yang C (2006) Determination of the effective thermal diffusivity of nanofluids by the double hot-wire technique. J Phys D Appl Phys 39:5316–5322
7. Murshed SMS, Leong KC, Yang C (2008) Investigations of thermal conductivity and viscosity of nanofluids. Int J Therm Sci 47:560–568
8. Murshed SMS, Leong KC, Yang C (2008) Thermophysical and electrokinetic properties of nanofluids – a critical review. Appl Therm Eng 28:2109–2125
9. Yu W, France DM, Routbort JL, Choi SUS (2008) Review and comparison of nanofluid thermal conductivity and heat transfer enhancements. Heat Transf Eng 29:432–460
10. You SM, Kim JH, Kim KM (2003) Effect of nanoparticles on critical heat flux of water in pool boiling of heat transfer. Appl Phys Lett 83:3374–3376
11. Wen D, Ding Y (2004) Experimental investigation into convective heat transfer of nanofluids at the entrance region under laminar flow conditions. Int J Heat Mass Transf 47:5181–5188
12. Wen D, Ding Y (2005) Experimental investigation into the pool boiling heat transfer of aqueous based alumina nanofluids. J Nanopart Res 7:265–274
13. Bang IC, Chang SH (2005) Boiling heat transfer performance and phenomena of Al_2O_3-water nano-fluids from a plain surface in a pool. Int J Heat Mass Transf 48:2407–2419
14. Heris SZ, Etemad SG, Esfahany MS (2006) Experimental investigation of oxide nanofluids under laminar flow convective heat transfer. Int Commun Heat Mass Transf 33:529–535
15. Murshed SMS, Leong KC, Yang C, Nguyen NT (2008) Convective heat transfer characteristics of aqueous TiO_2 nanofluids under laminar flow conditions. Int J Nanosci 7:325–331
16. Murshed SMS, Milanova D, Kumar R (2009) An experimental study of surface tension-dependent pool boiling characteristics of carbon nanotubes-nanofluids. In: Proceedings of 7th

ASME international conference on nanochannels, microchannels and minichannels, Pohang, Korea, 2009
17. Choi SUS, Zhang Z, Yu W, Lockwood F, Grulke E (2001) Anomalous thermal conductivity enhancement in nanotube suspensions. Appl Phys Lett 79:2252–2254
18. Ding Y, Alias H, Wen D, Williams RA (2006) Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids). Int J Heat Mass Transf 49:240–250
19. Murshed SMS, Nieto de Castro CA, Lourenço MJV, Lopes MLM, Santos FJV (2011) A review of boiling and convective heat transfer with nanofluids. Renew Sustain Energy Rev 15:2342–2354
20. Ribeiro APC, Lourenço MJV, Nieto de Castro CA, Hardacre C (2008) Thermal conductivity of "Buck Gels". In: Proceedings conference on molten salts and ionic liquids (EUCHEM2008), Copenhagen, Denmark, 2008
21. Seddon KR (2003) Ionic liquids – a taste of the future. Nature 2:363–365
22. Marsh KN, Boxall JA, Lichtenthaler R (2004) Room temperature ionic liquids and their mixtures – a review. Fluid Phase Equilibr 219:93–98
23. Zhang S, Sun N, He X, Lu X, Zhang X (2006) Properties of ionic liquids: database and evaluation. J Phys Chem Ref Data 35:1475–1517
24. Keskin S, Kayrak-Talay D, Akman U, Hortacsu O (2007) A review of ionic liquids towards supercritical fluid applications. J Supercrit Fluid 43:150–180
25. Earle M, Seddon KR (2007) Ionic liquids. Green solvents for the future. Pure Appl Chem 72:1391–1398
26. Holbrey J (2007) Heat capacities of common ionic liquids – potential applications as thermal fluids. Chimica Oggi/Chem Today 25:24–26
27. Wasserscheid P, Welton T (2007) Ionic liquids in synthesis. Wiley-VCH, Weinheim
28. Gaune-Escard M, Seddon KR (2009) Molten salts and ionic liquids: never the twain. Wiley, Hoboken
29. Chiappe C, Pieraccini D (2005) Ionic liquids: solvent properties and organic reactivity. J Phys Org Chem B 18:275–297
30. Heintz A, Wertz C (2006) Ionic liquids: a most promising research field in solution chemistry and thermodynamics. Pure Appl Chem 78:1587–1593
31. Nieto de Castro CA, Santos FJV (2007) Measurement of ionic liquids properties. Are we doing it well? Chimica Oggi/Chem Today 25:20–23
32. França J, Nieto de Castro CA, Lopes MLM, Nunes VMB (2009) Influence of thermophysical properties of ionic liquids in chemical process design. J Chem Eng Data 54:2569–2575
33. Nunes VMB, Lourenço MJV, Santos FJV, Lopes MLM, Nieto de Castro CA (2010) Accurate measurements of physico-chemical properties on ionic liquids and molten salts. In: Seddon KR, Gaune-Escard M (eds) Ionic liquids and molten salts: never the twain. Wiley, Hoboken
34. Nieto de Castro CA, Langa E, Morais AL, Lopes MLM, Lourenço MJV, Santos FJV, Santos MSCS, Lopes JSL, Veiga HIM, Macatrão M, Esperança JMSS, Rebelo LPN, Marques CS, Afonso CAM (2010) Studies on the density, heat capacity, surface tension and infinite dilution diffusion with the ionic liquids [C_4mim][NTf_2], [C_4mim][dca], [C_2mim][$EtOSO_3$] and [aliquat][dca]. Fluid Phase Equilibr 294:157–179
35. Fukushima T, Kosaka A, Ishimura Y, Yamamoto T, Takigawa T, Ishii N, Aida T (2003) Molecular ordering of organic molten salts triggered by single-walled carbon nanotubes. Science 300:2072–2074
36. Fukushima T, Aida T (2007) Ionic liquids for soft functional materials with carbon nanotubes. Chem-Eur J 13:5048–5058
37. Vieira SIC, Ribeiro APC, Lourenço MJV, Nieto de Castro CA (2011) Paints with ionanofluids as pigments for improvement of heat transfer on architectural and heat exchangers surfaces. In: Proceedings of the 25th European symposium on applied thermodynamics, Saint Petersburg, Russia, 2011
38. Lide DR (2007) CRC handbook of chemistry and physics. Taylor & Francis, Boca Raton

39. França J (2010) Propriedades térmicas de ionanofluidos (Thermal properties of ionanofluids). MSc thesis, Faculdade de Ciências da Universidade de Lisboa, Portugal
40. Holbrey J, Seddon K, Wareing R (2001) A simple colorimetric method for the quality control of 1-alkyl-3-methylimidazolium ionic liquid precursors. Green Chem 3:33–36
41. Carslaw HS, Jaeger JC (1959) Conduction of heat in solids. Oxford University Press, London
42. Ge R, Hardacre C, Nancarrow P, Rooney D (2007) Thermal conductivities of ionic liquids over the temperature range from 293 K to 353 K. J Chem Eng Data 52:1819–1823
43. Nieto de Castro CA, Lourenço MJV, Sampaio MO (2000) Calibration of a DSC: its importance for the traceability and uncertainty of thermal measurements. Thermochimica Acta 347:85–91
44. Lourenço MJV, Santos FJV, Ramires MLV, Nieto de Castro CA (2006) Isobaric specific heat capacity of water and aqueous cesium chloride solutions for temperatures between 298 K and 370 K at p = 0.1 MPa. J Chem Thermodyn 38:970–974
45. Xie H, Lee H, Youn W, Choi M (2003) Nanofluids containing multiwalled carbon nanotubes and their enhanced thermal conductivities. J Appl Phys 94:4967–4971
46. Amrollahi A, Rashidi AM, Emani MM, Kashefi K (2009) Conduction heat transfer characteristics and dispersion behaviour of carbon nanofluids as a function of different parameters. J Exp Nanosci 4:347–363
47. Venerus DC, Kabadi MS, Lee S, Perez-Luna V (2006) Study of thermal transport in nanoparticle suspensions using forced Rayleigh scattering. J Appl Phys 100:094310–1–094310–5
48. Nieto de Castro CA, Lourenço MJV, Murshed SMS, Vieira SI, França J, Queiros CS, Ribeiro APC (2010) Ionanofluids: new heat transfer fluids for thermal efficiency design. In: Proceedings of the 9th Asian thermophysical properties conference, Beijing, China, 2010
49. Ge R, Hardacre C, Jacquemin J, Nancarrow P, Rooney D (2008) Heat capacities of ionic liquids as a function of temperature at 0.1 MPa. Measurement and prediction. J Chem Eng Data 53:2148–2153
50. Mendonça AJF, Nieto de Castro CA, Assael MJ, Wakeham WA (1981) The economic advantages of accurate transport property data for heat transfer equipment design. Rev Port Quím 23:7–11
51. Lopes MLM, Nieto de Castro CA, Wakeham WA (1985) The effect of uncertainty in diffusion coefficients in the design of packed columns. In: Proceedings of the international chemical engineering conference, Coimbra, Portugal
52. Nunes VMB, Lourenço MJV, Santos FJV, Nieto de Castro CA (2003) The importance of the accurate data on viscosity and thermal conductivity in molten salts applications. J Chem Eng Data 48:446–450