

Rheological and heat transfer behaviour of the ionic liquid, [C₄mim][NTf₂]

Haisheng Chen ^a, Yurong He ^a, Jianwei Zhu ^a, Hajar Alias ^a, Yulong Ding ^{a,*},
Paul Nancarrow ^b, Christopher Hardacre ^b, David Rooney ^{b,*}, Chunqing Tan ^c

^a Institute of Particle Science and Engineering, University of Leeds, Leeds LS2 9JT, UK

^b QUILL Research Centre and School of Chemistry and Chemical Engineering, Queen's University, Belfast BT9 5AG, UK

^c Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100080, China

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Abstract

Systematic experiments have been carried out on the thermal and rheological behaviour of the ionic liquid, 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [C₄mim][NTf₂], and, *for the first time*, on the forced convective heat transfer of an ionic liquid under the laminar flow conditions. The results show that the thermal conductivity of the ionic liquid is $\sim 0.13 \text{ W m}^{-1} \text{ K}^{-1}$, which is almost independent of temperature between 25 and 40 °C. Rheological measurements show that the [C₄mim][NTf₂] liquid is a Newtonian fluid with its shear viscosity decreasing with increasing temperature according to the exponential law over a temperature range of 20–90 °C. The convective heat transfer experiments demonstrate that the thermal entrance length of the ionic liquid is very large due to its high viscosity and low thermal conductivity. The convective heat transfer coefficient is observed to be much lower than that of distilled water under the same conditions. The convective heat transfer data are also found to fit well to the convectional Shah's equation under the conditions of this work.

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1. Introduction

Ionic liquids are organic salts of low melting points with a wide range of liquidus temperature and some highly desirable characteristics such as low vapour pressure, high thermal stability, ionic conductivity and a large electrochemical window (Wasserschied and Welton, 2002; Kim et al., 2005; Zhou, 2005; Earle et al., 2006). These intrinsically useful characteristics have led to ionic liquids being regarded as 'greener' alternatives to volatile organic solvents with the potential to be recyclable and hence have

been generating increasing interest over the past decade. Numerous studies have been carried out on developing new ionic liquids and the list of ionic liquid grows on daily basis (Welton, 2004). In parallel, there has been a significant growth in the use of ionic liquids in various processes, including liquid–liquid extraction of organics from water and metal ions from solution, separation of isomeric organic compounds, selective catalytic processes for organic chemical reactions, and solar cells and other electrochemical devices, synthesis of inorganic nanomaterials, and serving as a catalyst or a co-catalysts and a ligand source (Welton, 2004; Kabo et al., 2004; Zhou, 2005; Troncoso et al., 2006).

In comparison with the work on the synthesis and use of ionic liquids, there have been fewer studies concerning the measurement of their basic physical and transport properties. This is particularly true for the thermal properties.

* Corresponding authors. Tel.: +44 (0) 113 343 2747; fax: +44 (0) 113 343 2405 (Y. Ding); tel.: +44 (0) 28 90974050; fax: +44 (0) 28 90974687 (D. Rooney).

E-mail addresses: y.ding@leeds.ac.uk (Y. Ding), d.rooney@qub.ac.uk (D. Rooney).

Nomenclature

<i>a</i>	thermal diffusivity	<i>T_f</i>	fluid temperature
<i>A</i>	cross-sectional area of the test section	<i>T_{in}</i>	fluids inlet temperature
<i>c_p</i>	heat capacity of fluid	<i>T_w</i>	wall temperature
<i>D</i>	test tube inner diameter	<i>u</i>	fluid velocity
<i>h</i>	convective heat transfer coefficient	<i>x</i>	axial position
<i>k</i>	thermal conductivity	<i>x[*]</i>	dimensionless $x = x/D$
<i>Nu</i>	Nusselt number		
<i>Pr</i>	Prandtl number		
<i>q</i>	heat flux		
<i>Re</i>	Reynolds number		
<i>S</i>	perimeter of the test tube		

<i>Greek symbols</i>			
ρ	fluids density		
μ	fluid viscosity		
ν	fluid kinematic viscosity		

Although some heat capacity and heat of solution measurements have been reported (Crosthwaite et al., 2005; Holbrey et al., 2003; Shimizu et al., 2006; Waliszewski et al., 2005) the data concerning thermal conductivity and thermal diffusivity is limited to only a few points (Frez et al., 2006; Van Valkenburg et al., 2005) and no reports, to date, have shown the convective heat transfer behaviour of ionic liquids under the flow conditions. This forms the driver for carrying out this work on measuring the thermal and rheological properties of ionic liquids and on investigating the forced convective heat transfer of ionic liquids. These are needed for industrial take-up of the technology particularly process development and scale-up. $[\text{C}_4\text{mim}]\text{[NTf}_2]$ was used as the model ionic liquid in this work as it is both air and moisture stable and has a viscosity and density which is suitable for use in standard laboratory equipment. The physical properties, as well as ease of handling, for this particular ionic liquid are expected to provide it with a wide range of applications in the near future (Troncoso et al., 2006).

2. Experimental

2.1. Synthesis of the ionic liquid ($[\text{C}_4\text{mim}]\text{[NTf}_2]$)

$[\text{C}_4\text{mim}]\text{[NTf}_2]$ was synthesized in two steps. The first step was to synthesize the 1-Butyl-3-methylimidazolium bromide ($[\text{C}_4\text{mim}]\text{Br}$). This was initially done by adding 10% excess of 1-bromobutane (Sigma Aldrich, 99 +%) to 1-methylimidazole (Sigma Aldrich, 99%) and heating to 70 °C under reflux, until the 1-methylimidazole was completely reacted. The formation of $[\text{C}_4\text{mim}]\text{Br}$ was confirmed by testing for unreacted 1-methylimidazole with CuCl_2 solution (Holbrey et al., 2001). The $[\text{C}_4\text{mim}]\text{Br}$ was then washed five times with ethyl acetate to remove any traces of starting material. Finally, the remaining solvent was removed using a rotary evaporator, followed by drying under high vacuum at 90 °C.

The $[\text{C}_4\text{mim}]\text{[NTf}_2]$ ionic liquid, was synthesized from $[\text{C}_4\text{mim}]\text{Br}$ and $\text{Li}[\text{NTf}_2]$ (3 M, 99%) by a metathesis reaction. Equimolar amounts of each component were first dis-

solved in distilled water. The two solutions were added together and mixed vigorously for at least 12 h. After reaction, dichloromethane (DCM) was added to dissolve the product, $[\text{C}_4\text{mim}]\text{[NTf}_2]$, and the mixture was allowed to settle into two phases. The organic phase was separated from the aqueous phase, and washed five times with distilled water to remove any residual LiBr. Finally the DCM was removed using a rotary evaporator at 50 °C, and the remaining $[\text{C}_4\text{mim}]\text{[NTf}_2]$ was dried under high vacuum at 70 °C for 4–5 h.

^1H NMR was used to confirm that the $[\text{C}_4\text{mim}]\text{[NTf}_2]$ was free of DCM or organic starting materials. Water content was determined by the Karl-Fischer analysis to be <0.05 wt%. The halide content was determined using ion chromatography (Villagran et al., 2004), and found to be below the detection limit of 5 ppm.

2.2. Measurement of the thermal conductivity

The thermal conductivity was measured by using a KD2 thermal property meter (Labcell Ltd., UK), which is based on the transient hot wire method. The KD2 meter has a probe with 60 mm length and 0.9 mm diameter, which integrates in its interior a heating element and a thermo-resistor, and is connected to a microprocessor for controlling and conducting the measurements. The KD2 meter was calibrated by using distilled water and standard oil before any set of measurements. In order to study the effect of temperature, a thermostat bath (GD 120-S12, Grant, UK) was used, which was able to maintain the temperature uniformity within 0.1 K. At least five measurements were taken for each temperature to ensure the uncertainty of measurements within 3%.

2.3. Measurement of the rheological behaviour

The rheological behaviour of $[\text{C}_4\text{mim}]\text{[NTf}_2]$ was studied by using a Bohlin CVO rheometer (Malvern Instruments, UK). The measurements were based on the controlled shear stress model with the shear rate ranging between ~ 1 and $10,000 \text{ s}^{-1}$. Calibrations were conducted against

standard solutions on weekly basis over the duration of this work to ensure accurate measurements. Three measurements were taken for each test and the maximum uncertainty of viscosity measurements was found to be $\sim 1.7\%$.

2.4. Measurement of the forced convective heat transfer coefficient

2.4.1. Experimental system

The experimental system for measuring the convective heat transfer coefficient is shown schematically in Fig. 1. It consisted of a flow loop, a heat unit, a cooling part, and a measuring and control unit. The flow loop included a pump with a built-in flowmeter, a reservoir, a collection tank and a test section. A straight copper tube with 2 m length, 3.97 mm inner diameter and 6.35 mm outer diameter was used as the test section. The whole test section was heated by two flexible silicon rubber heaters (Watlow, UK) with 917 mm heating length each, which were linked to a DC power supply (TTi Ex 752 m, RS, UK). The power supply was adjustable and had a maximum power supply of 300 W. There was a thick thermal isolating layer surrounding the heater to obtain a constant heat flux condition along the test section. Nine T-type thermocouples were mounted on the test section at an axial interval of 200 mm from the inlet of the test section to measure the wall temperature distribution, and two further T-type thermocouples were inserted into the flow at the inlet and exit of the test section to measure the bulk temperature of the fluid. The pump was of a peristaltic type with the flowrate controlled by the rotational rate. The maximum flowrate the pump could deliver was 10 l per minute. There was a three-way valve in the flow loop for flowrate calibrations and flow system cleaning. In the experiments, the pump rotational rate, voltage and current of the DC power supply were recorded; the temperature readings from the 11

thermocouples were registered by a data requisition system. The flowrate of the fluid was calibrated by a weighing method as the pump performance was sensitive to the fluid viscosity which could give an accuracy of flowrate better than $\sim 4\%$. The thermocouples were calibrated in a thermostatic water bath and the accuracy was found to be within 0.2 K.

Note that before any convective heat transfer experiments, tests were conducted on experimental rig to investigate possible chemical reactions between the ionic liquid with the wall materials used in the construction of the rig. No significant changes were found to the ionic liquid after these materials were soaked in the liquid for a period of up to 10 days.

2.4.2. Data processing

The measured temperature data and heat flux were used to calculate the convective heat transfer coefficient (h) defined as

$$h(x) = q/(T_w(x) - T_f(x)) \quad (1)$$

where x represents axial distance from the entrance of the test section, q is the heat flux, T_w is the measured wall temperature, and T_f is the fluid temperature determined by the following energy balance:

$$T_f(x) = T_{in} + qSx/(\rho c_p u A) \quad (2)$$

with c_p the heat capacity, ρ the fluid density, T_{in} is the inlet fluid temperature, A and S respectively the cross-sectional area and perimeter of the test tube, and u the average fluid velocity. Eq. (2) is based on the assumption of zero heat loss through the insulation layer. The deviation from this assumption was assessed by comparing the measured temperature difference between inlet and outlet of the test section with the theoretical value calculated by Eq. (2). It was found that the maximum deviation was lower than 4% under the conditions employed in this work. The uncertainty of the heat transfer coefficient was estimated to be better than $\sim 6.4\%$.

3. Results and discussion

3.1. Thermal conductivity of the ionic liquid

Fig. 2 shows the thermal conductivity of $[C_4mim][NTf_2]$ as a function of temperature. It can be seen that the thermal conductivity of $[C_4mim][NTf_2]$ is $\sim 0.13 \text{ W m}^{-1} \text{ K}^{-1}$ and is almost independent of temperature over the range investigated. This indicates that $[C_4mim][NTf_2]$ is a relatively poor thermal conductor with the thermal conductivity approximately $\sim 22\%$ of that of water at the room temperature. Initially, the temperature-independent thermal conductivity of the $[C_4mim][NTf_2]$ was thought to be due to the inappropriate method of measurements as both the thermal probe and the liquid are electrically conductive. This possibility was excluded by using a thermal probe coated with a thin coating of an insulator. It was also

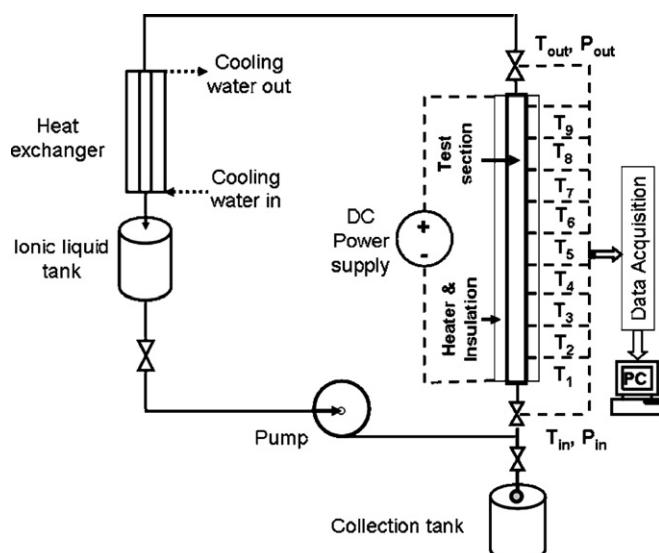


Fig. 1. Experimental system for the convective heat transfer experiments.

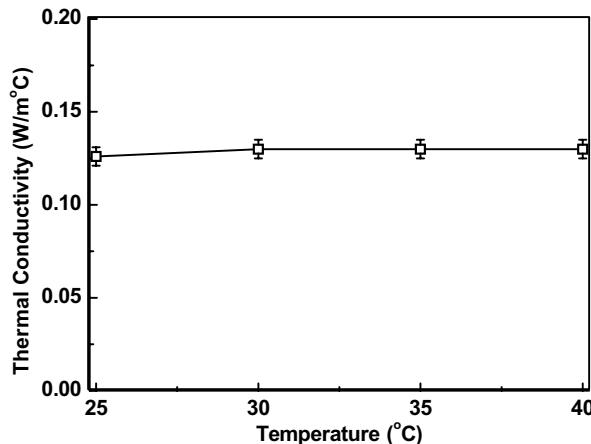


Fig. 2. Effective thermal conductivity of $[C_4mim][NTf_2]$.

hypothesised that the temperature-independent behaviour is associated with the high viscosity of the liquid. As will be seen in the following section, this is unlikely to be a dominant reason as the viscosity changes significantly with changing temperature. It is noted that Van Valkenburg et al. (2005) measured the thermal conductivities of three ionic liquids, $[C_2mim][BF_4]$, $[C_4mim][BF_4]$ and $[C_3dmim][NTf_2]$ (1,2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide), over a temperature range of 27–117 °C using a similar method to that used in this work. Therein, the thermal conductivities of $[C_2mim][BF_4]$, $[C_4mim][BF_4]$ and $[C_3dmim][NTf_2]$ were found to decrease slightly with increasing temperature, the variation of which is given by the equations $-(12.1 \pm 1.5) \times 10^{-5} \cdot T + (0.235 \pm 0.005)$, $-(6.13 \pm 0.11) \times 10^{-5} \cdot T + (0.204 \pm 0.004)$ and $-(4.61 \pm 0.79) \times 10^{-5} \cdot T + (0.144 \pm 0.004)$, respectively, where the units of temperature are K and the thermal conductivity are $W\ m^{-1}\ K^{-1}$. Given the experimental error, the temperature dependence is negligible, in good agreement with the results shown in Fig. 2. Furthermore, for $[C_3dmim][NTf_2]$ at 25 °C, the thermal conductivity was found to be $0.131\ W\ m^{-1}\ K^{-1}$ which correlates well with the value of $0.13\ (\pm 0.005)\ W\ m^{-1}\ K^{-1}$ at 25 °C for $[C_4mim][NTf_2]$ observed in the present case 0.126.

3.2. Rheological behaviour of $[C_4mim][NTf_2]$

Fig. 3a shows the shear rate as a function of shear stress for $[C_4mim][NTf_2]$ at 25 °C and 40 °C. The linear relationships between the shear rate and shear stress suggest Newtonian behaviour of the ionic liquid at the two temperatures. Fig. 3b shows that the shear viscosity at 25 °C is approximately two times that at 40 °C, indicating a strong temperature effect on the fluid. This is demonstrated more clearly in Fig. 4 where the shear viscosity is plotted against temperature. Regression of the data shows that the shear viscosity depends on temperature in an exponential manner as follows:

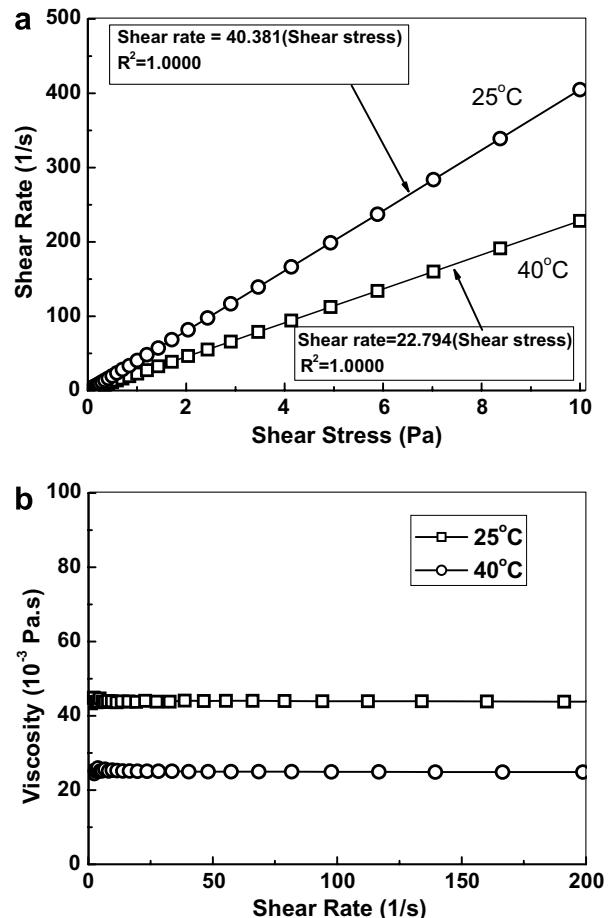


Fig. 3. Rheological behaviour of $[C_4mim][NTf_2]$: (a) shear rates as a function of shear stress at 25 °C and 40 °C and (b) Viscosity of as a function of shear rate at 25 °C and 40 °C.

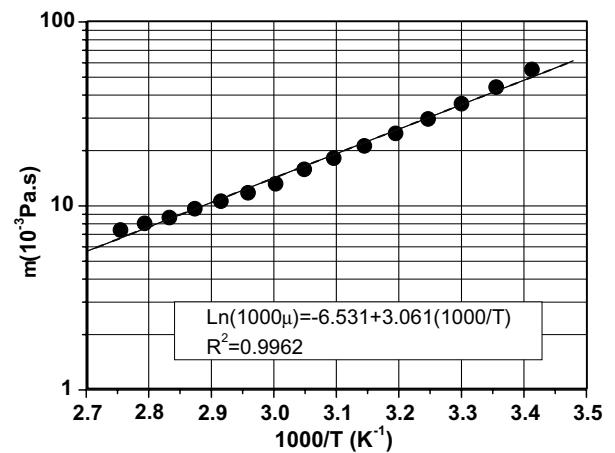


Fig. 4. Viscosity of $[C_4mim][NTf_2]$ as a function of temperature.

$$\mu = 10^{-3} \exp \left[-6.531 + 3.061 \times \frac{1000}{T} \right] \quad (3)$$

Eq. (3) is consistent with the widely used empirical expression for liquid viscosity (Bird et al., 2002) and the thermodynamic scaling relationship for van der Waals,

H-bonded and ionic liquids (Roland et al., 2006). The strong temperature dependence of the shear viscosity is very much different from the thermal conductivity as discussed in Section 3.1, indicating that the thermal (transport) properties of the ionic liquid cannot be linked directly to its momentum properties. The viscosities measured here are in agreement with those measured previously (Bonhôte et al., 1996) which measured the viscosity as 53 cP at 20 °C.

3.3. Convective heat transfer coefficient

Prior to the systematic experiments with $[C_4mim][NTf_2]$, the experimental system was tested with distilled water to evaluate the repeatability and accuracy of the measurements in the laminar flow regime. The data were found to compare well with the published data in the literature for water and the well-known Shah's equation for forced convective heat transfer in the laminar flow regime (Shah and London, 1978), where the Shah's equation takes the following form:

$$Nu(x) = \begin{cases} 1.302(x^*)^{-1/3} - 1 & x^* \leq 0.00005 \\ 1.302(x^*)^{-1/3} - 0.5 & 0.00005 < x^* \leq 0.0015 \\ 4.364 + 8.68(10^3 x^*)^{-0.506} e^{-41x^*} & 0.00005 \leq x^* \leq 0.0015 \end{cases} \quad (4)$$

where x^* is defined as $x/(DRePr)$, Re is the Reynolds number defined as $Re = \rho u D / \mu$ with D the pipe inner diameter and μ the fluid viscosity, Pr is the Prandtl number given by $Pr = \nu / \alpha$ with ν the fluid kinematic viscosity and α the fluid thermal diffusivity, and Nu is the Nusselt number defined as $Nu(x) = h(x)D/k$ with k the thermal conductivity of the fluid. Eq. (4) was reported to be applicable to the entire laminar flow regime ($0 < Re < 2300$) with a maximum error of $\pm 1.0\%$ (Shah and London, 1978).

Having established the confidence in the experimental system, systematic experiments were conducted on the ionic fluid under the laminar flow conditions. Fig. 5 shows the typical temperature profiles along the test section at

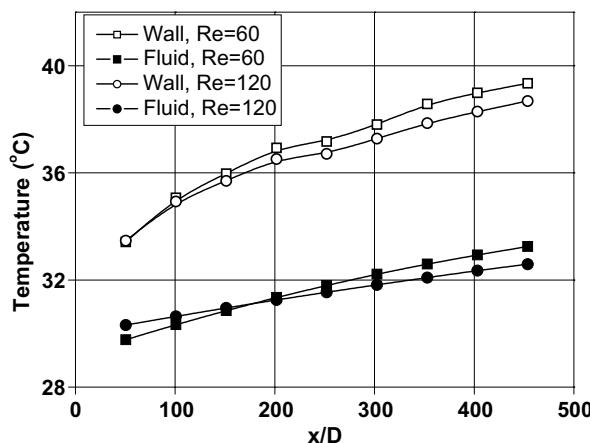


Fig. 5. Temperature profiles along the test section.

two Reynolds numbers. As expected, due to the constant wall heat flux, the fluid temperature increases with increasing axial position. The temperature data are used to obtain the convective heat transfer coefficient and the Nusselt number. Fig. 6a shows the Nusselt number of the ionic liquid as a function of axial distance at four different Reynolds numbers. For a given Reynolds number, the Nusselt number decreases with increasing axial distance, which can be explained to be due to the entrance effect. At a given axial position, the Nusselt number increases with increasing Reynolds, which can also be explained in a similar way, a higher Reynolds number gives a thinner boundary layer hence a higher convective heat transfer coefficient. On a quantitative basis, the flow of a Newtonian fluid is hydrodynamically fully developed at $x/D > \sim(0.05Re)$, and is thermally fully developed at $x/D > \sim(0.05RePr)$ (Bird et al., 2002). Given the range of the Reynolds number considered in this work, the entrance length in terms of the fluid hydrodynamics is in the range of $x/D = 3–6$. However, the thermal entrance length is very large mainly because of low thermal conductivity and high viscosity. Under the experimental conditions of this work, the viscosity of the ionic liquid can be taken approximately as

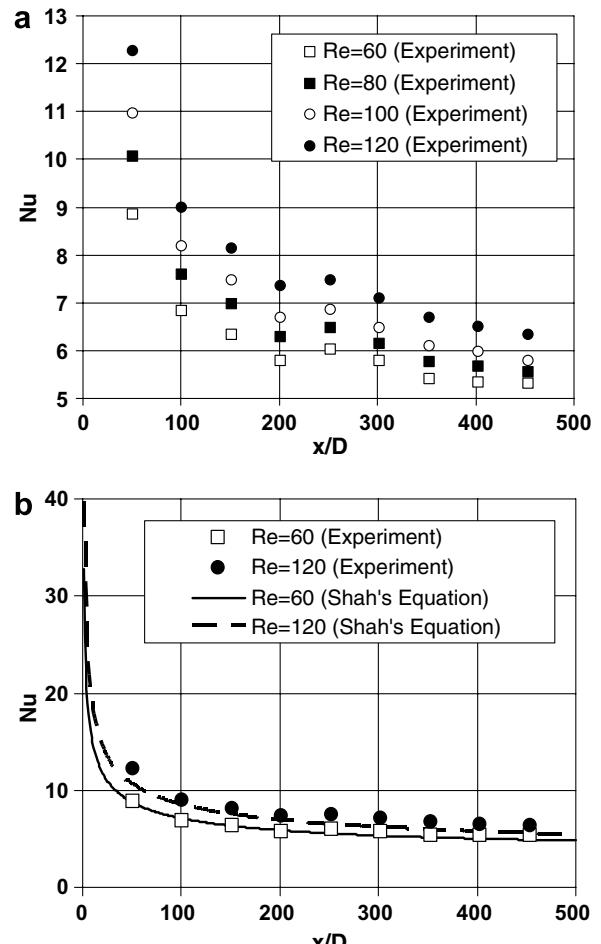


Fig. 6. Heat transfer behaviour of $[C_4mim][NTf_2]$ along axial direction: (a) experimental data and (b) comparison with Shah's equation.

0.0359 Pa s (Figs. 4 and 5), the heat capacity of the ionic liquid is $1365 \text{ J kg}^{-1} \text{ K}^{-1}$ (Troncoso et al., 2006), and the thermal conductivity is $0.13 \text{ W m}^{-1} \text{ K}^{-1}$ (Section 3.1). These data give a Prandtl number of approximately 370. The thermal entrance length can, therefore, be estimated as 1100–2200. The test section used in this work only gives a maximum value of $x/D = \sim 453$. The thermal boundary layer is therefore not fully developed. This can actually be seen from Fig. 6a. Fig. 6b compares the experimental results with the predictions by Eq. (4). Excellent agreement has been obtained, suggesting that Shah's equation could be used to predict the forced convective heat transfer of Newtonian ionic liquids under the laminar flow conditions.

Figs. 7a and b compare the convective heat transfer coefficient of the ionic liquid with that of distilled water for $Re=100 \pm 5$. It can be seen that the Nusselt number of water decays with increasing axial position and the Nusselt number of the ionic liquid is much higher than that of distilled water at small x/D (Fig. 7a). The difference decreases with increasing x/D and is expected to diminish at x/D greater than the thermal entrance length of the ionic liquid. However, the actual convective heat transfer coefficient of the ionic liquid is much lower than that of water

(Fig. 7b). At $x/D = 143$, the ratio of the Nusselt number of water to that of the ionic liquid is approximately 3.88 (Fig. 7b), which is lower than the corresponding thermal conductivity ratio of ~ 4.61 ($0.6/0.13$). This again is an indication that the thermal boundary has not been fully developed.

4. Concluding remarks

The thermal and rheological properties of $[\text{C}_4\text{mim}]\text{[NTf}_2]$ has been characterized for the first time including its convective heat transfer behaviour under the laminar flow region. The following conclusions are obtained:

- The thermal conductivity of the ionic liquid is $\sim 0.13 \text{ W m}^{-1} \text{ K}^{-1}$, which is $\sim 22\%$ of that of water and is almost independent of temperature over the temperature range studied.
- The ionic liquid shows Newtonian behaviour under the conditions of this work with its shear viscosity decreasing with increasing temperature. The temperature dependence takes an exponential form over the temperature range of 20–90 °C.
- The convective heat transfer data correlates well with the conventional Shah's equation in the laminar flow region tested.
- The convective heat transfer coefficient of the ionic liquid is much lower than that of distilled water under the same conditions.

The conclusions obtained in this work apply to $[\text{C}_4\text{mim}]\text{[NTf}_2]$, one of the most frequently used ionic liquids, over the temperature range investigated. Future work will focus on investigating other commonly used ionic liquids, to determine the widespread applicability of these conclusions, and to provide an understanding of the behaviour of ionic liquids under a variety of heat transfer conditions.

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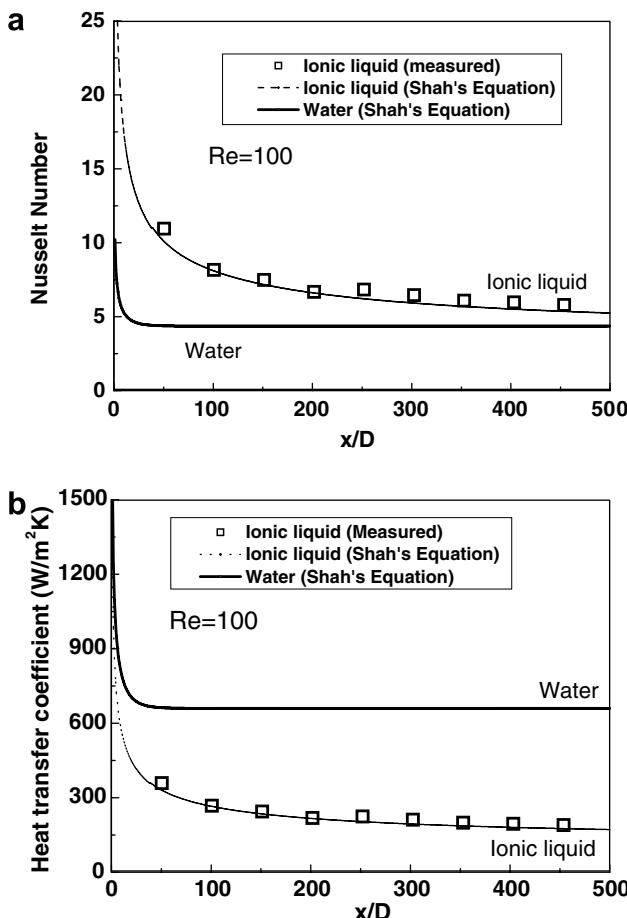


Fig. 7. Comparison of the convective heat transfer between the ionic liquid and water: (a) Nusselt number and (b) heat transfer coefficient.

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