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## Effect of nanoparticle dispersion on thermophysical properties of ionic liquids for its potential application in solar collector

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### Abstract

Concentrated Solar Power (CSP) is one of the developing alternative energy technology, where mirror or lenses are used to concentrate sunlight from a large area and stored in collector filled with heat transfer fluid (HTF). The stored energy from HTF is then used to produce steam for power generation. Nanoparticle Enhanced Ionic Liquids (NEILs), inclusion of nanoparticles into Ionic Liquids (ILs), are considered as a potential HTF for CSP applications. In this present paper, we have experimentally investigated the density, rheological behavior, and thermal conductivity of NEILs forming with N-butyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide ( $[N_{4111}][NTf_2]$ ) IL and 1 wt%  $Al_2O_3$  nanoparticles (spherical and whiskers) and carbon black. The experimental results show that NEILs with whisker-shape nanoparticles show highest thermal conductivity enhancement, which is ~7%. The rheological behavior of NEILs shows the shear thinning behavior occurs at all the measured temperatures and the shear thinning increases with temperature. The inclusion of nanoparticles into ILs enhances the viscosity compared to the base IL and it is highly dependent on the temperature, where viscosity sharply decreases with the increase of temperature. The possible mechanisms of this enhancement are discussed in the paper.

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**Keywords:** Concentrated Solar Power; Nanoparticle; Nanoparticle Enhanced Ionic Liquids (NEILs); Thermal Conductivity; Rheological Behavior.

### 1. Introduction

Nowadays global world is in real crisis of environmental friendly and efficient energy sources [1]. Solar energy is one of the most abundant sources of energy in the world. Solar energy can be harvested by means of direct

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conversion of sunlight into energy with photovoltaic effect which is called solar cell and by absorbing heat from the sunlight which is called solar thermal collector [2]. One of the forms of solar thermal collector is concentrated solar power (CSP) which is the growing technologies for electricity generation. In CSP system, electricity is generated by utilizing solar thermal energy through concentrating sunlight and using thermodynamic Rankine cycle, which needs high operating temperature heat transfer fluid (HTF) [3].

Nanoparticle enhanced ionic liquids (NEILs) have gained attention as a HTF for CSP applications, which is formulated by dispersion of small amount of nanoparticles in the base ionic liquids (ILs) [4]. The base ILs are the organic salts having low melting points (below 100°C), which are already considered as a potential candidate for HTF in solar thermal collector and potential replacement of several organic solvents in chemical industry for reaction and separation systems [5-8]. The great interests of ILs are because of their excellent physical and chemical properties including negligible vapor pressure, high thermal stability, high ionic conductivities, high solvating capability, and exposure to air and moisture stability [9-12]. However, the thermophysical properties of ILs can be enhanced by dispersing nanoparticles to form NEILs and there are several research groups working on the ILs based nanofluids. J. M. P. França et al. [13], C.A. Nieto de Castro et al. [14-15] and S. M. S. Murshed et al. [16] studied several imidazolium and pyrrolidinium ILs based IoNanofluids; reported ~9% thermal conductivity enhancement for 0.01 mass fraction of multi wall carbon nanotubes (MWCNTs) and ~8% heat capacity enhancement for 0.01 and 0.015 mass fraction of Baytubes. T. C. Paul et al. [17] have recently reported enhanced heat transfer coefficient of 0.5 wt% NEILs made with 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([C<sub>4</sub>mim][NTf<sub>2</sub>]) IL and Al<sub>2</sub>O<sub>3</sub> nanoparticles. N. J. Bridges et al. [11] have studied the heat capacity and thermal stability of NEILs made of 1-Butyl-2,3-dimethylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([C<sub>4</sub>mmim][NTf<sub>2</sub>]) IL with Al<sub>2</sub>O<sub>3</sub> and carbon black (CB) nanoparticles; have reported higher heat capacity values for Al<sub>2</sub>O<sub>3</sub> NEILs and lower heat capacity of CB NEILs. B. Wang et al. [19-21] studied the thermal conductivity, rheological and tribological behavior of 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF<sub>6</sub>]) IL based nanofluids with different size gold nanoparticle [19], gold nanoparticles with different stabilizing agents [20], and functionalized MWCNTs [21]; reported enhanced thermal conductivity, shear thinning behavior and favorable friction-reduction properties of nanofluids compare to base IL.

In the present study we report the thermophysical properties of NEILs containing N-butyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide ([N<sub>4111</sub>][NTf<sub>2</sub>]) IL and 1 wt% Al<sub>2</sub>O<sub>3</sub> nanoparticles (spherical and whiskers) and carbon black (CB). Also, the study gives an idea of nanoparticle shape effect on the thermophysical properties of NEILs.

## 2. Experimental methods

### 2.1. Material and synthesis of NEILs

1% (wt/wt) NEILs were prepared by N-butyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide ([N<sub>4111</sub>][NTf<sub>2</sub>]) IL with Al<sub>2</sub>O<sub>3</sub> (spherical and whiskers shape) and carbon black (CB) nanoparticles. 99% pure [N<sub>4111</sub>][NTf<sub>2</sub>] IL was purchased from IoLiTec Company (Germany). The chemical structure of the anion, cation, and the molecular formula of the IL are as follows:



Fig. 1. Chemical structure of cation and anion of [N<sub>4111</sub>][NTf<sub>2</sub>] IL

Molecular formula: C<sub>11</sub>H<sub>20</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>



Fig. 2. SEM image of  $\text{Al}_2\text{O}_3$  nanoparticles (a) spherical; (b) whiskers.

$\text{Al}_2\text{O}_3$  nanoparticles were purchased from Sigma-Aldrich, USA. Spherical shape nanoparticles are  $\gamma$ -phase with particle size  $< 50\text{nm}$  (TEM) and surface area  $> 40\text{ m}^2/\text{g}$  (BET); whiskers nanoparticles having diam.  $\times$  L,  $2\text{-}6\text{ nm} \times 200\text{-}400\text{ nm}$  and aspect ratio  $> 100$  (TEM).  $\text{Al}_2\text{O}_3$  nanoparticles was dispersed into the base IL by using vortex mixture. NEILs were processed for around 90 min in the vortex to break possible aggregations of nanoparticles. SEM image of the spherical and whiskers  $\text{Al}_2\text{O}_3$  nanoparticles are presented in Fig. 2(a) and (b) respectively.

## 2.2. Thermophysical property measurements

The density of base IL and NEILs were measured using a 1 mL Pycnometer from Thomas Scientific. The pycnometer and the samples were placed in a thermal bath (Thermo NESLAB) to maintain a uniform temperature. The weight of the sample was measured by using METTLER TOLEDO balance which has a precision of 0.01 mg. Before using for nanofluids the pycnometer was calibrated with water and was found to be accurate to within 0.5%.

Viscosity of the base IL and NEILs were measured using a cone and plate type rotary viscometer (LVDV-II+ProCP, from Brookfield Engineering Co.). The sample size required for the cone and plate arrangement is 1mL. The cone and plate arrangement has a thermal jacket to maintain constant sample temperature within accuracy of  $\pm 0.1^\circ\text{C}$ . The viscometer was calibrated using standard oil.

Thermal conductivity of the base IL and NEILs were measured using KD2 Pro thermal property analyzer (Decagon Device, USA). The measurements principle is based on the transient hot wire method. The meter has a probe of 60 mm length and 1.3 mm diameter with a heating element and a thermoresistor which is inserted vertically into the test sample. The probe is connected to a microcontroller for controlling and conducting the measurements. Before using for base IL and NEIL, the meter was calibrated with distilled water and standard glycerin. A thermal bath (Thermo NESLAB) was used to maintain constant temperature of the measuring sample. Temperature accuracy of the bath was within  $\pm 0.01\text{ K}$ .

## 3. Results and Discussion

### 3.1. Density of NEILs

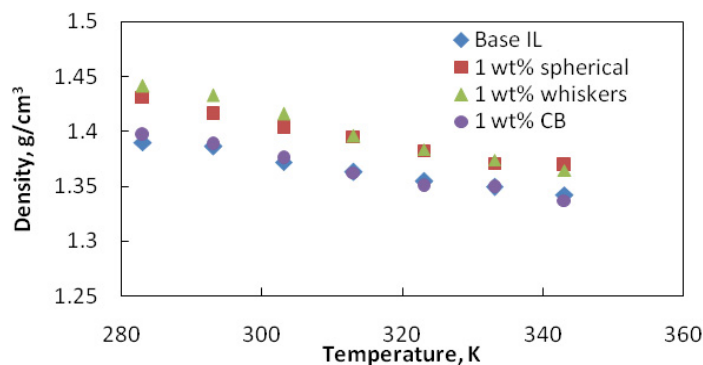


Fig.3. Density of base IL and NEILs as a function of temperature.

The density of base IL and 1 wt% NEILs as a function of temperature is presented in Fig. 3. Density of base IL and NEILs decreases with temperature within the measured temperature 283-343K. It is clear from Fig. 3 that the whiskers NEIL has higher density compare to spherical NEIL at low temperature and CB NEIL has the lowest density of all NEILs because of the lower density CB dispersion on IL compare to the  $\text{Al}_2\text{O}_3$  nanoparticles.

### 3.2. Rheological behavior of NEILs

Fig. 4(a) shows the rheological behavior of base IL and 1 wt% NEILs at 30°C temperature, which represents the shear viscosity as a function of shear rate and showing shear thinning behavior of NEILs, means shear viscosity decreases with shear rate. The shear thinning behavior occurs at all the measured temperatures and the shear thinning increases with temperature as shown in Fig. 4(b), where rheological behavior of 1 wt% spherical NEILs are presented at different temperature. Fig. 4(a) also shows that the CB NEILs has much higher viscosity compare to  $\text{Al}_2\text{O}_3$  NEILs which is clearer from Fig. 4 (c), where shear viscosity is presented as a function of temperature. This is because the CB has higher pore surface area on IL and generates more gel behavior [22]. It can be seen from Fig. 4(c) that viscosity decreases sharply with temperature over the measured temperature range. If we see the particle shape effect, spherical NEILs shows higher viscosity than whiskers  $\text{Al}_2\text{O}_3$  NEILs which contradict with previous study of conventional water- $\text{Al}_2\text{O}_3$  nanofluids with different shape of nanoparticles by E. V. Timofeeva et al. [22], and reported that nanofluids with rodlike nanoparticles shows higher viscosity; because restriction of rotational and translational Brownian motion of nanoparticles shows lower shear thinning behavior as well as higher viscosity. However, the experimental viscosity values of NEILs are consistent with the previous measurements [18, 22, and 24], where they studied NEILs forming with other ILs and nanoparticles.

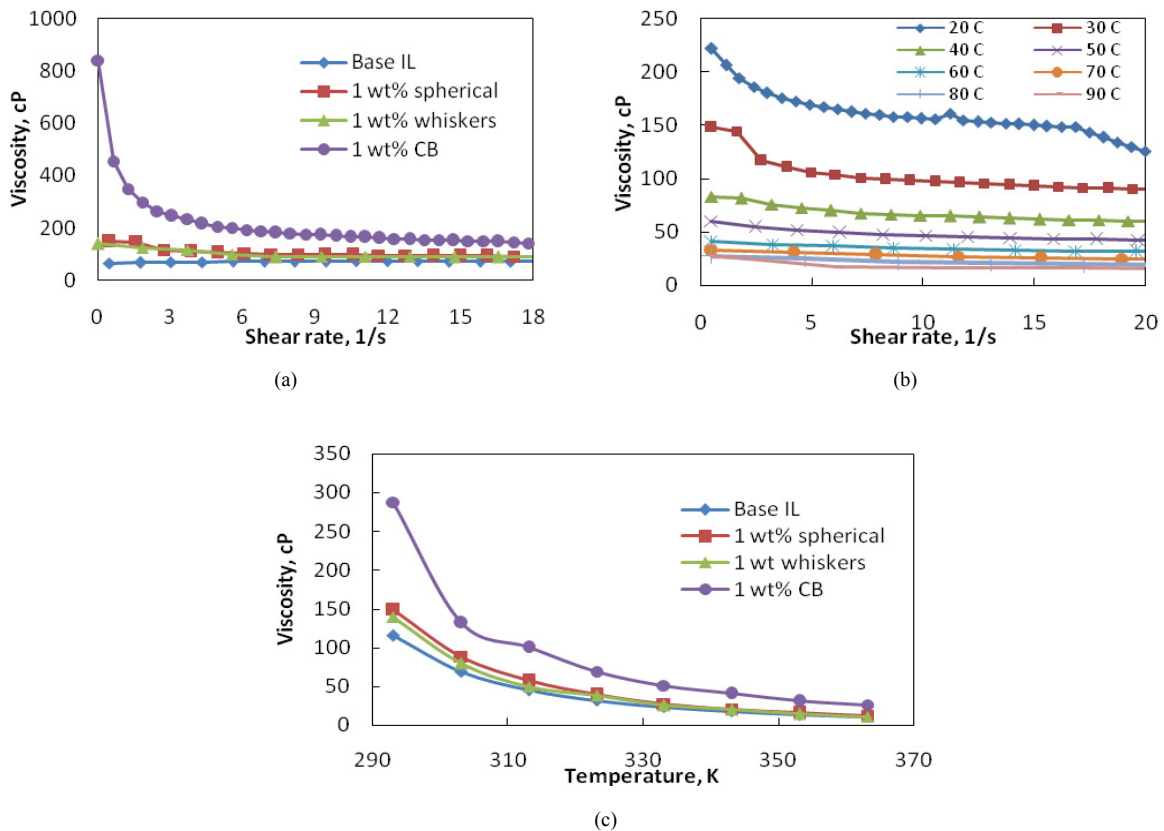


Fig. 4. Rheological behavior of base IL and NEILs at temperature (a) 30°C; (b) spherical  $\text{Al}_2\text{O}_3$  NEILs at different temperature; (c) Viscosity as a function of temperature.

### 3.3. Thermal conductivity of NEILs

Thermal conductivity of base IL and 1 wt% different NEILs as a function of temperature is shown in Fig. 5(a). Thermal conductivity of  $\text{Al}_2\text{O}_3$  NEILs shows enhancement but CB NEILs shows decrease in thermal conductivity compare to base IL. Also for same nanoparticles spherical shape shows  $\sim 5\%$  and whiskers shape shows  $\sim 7\%$  enhancement, which is clearer in the Fig. 5(b), where thermal conductivity of NEILs are normalized with respect to the corresponding thermal conductivity of base IL. This is because increasing particle aspect ratio has positive effect on thermal conductivity enhancement [23]. For traditional water or ethylene glycol based nanofluids the possible mechanism of thermal conductivity enhancement are Brownian motion of nanoparticles, liquid layering in liquid/nanoparticle surface interface, nature of heat transport to the nanoparticles, and the effect of nanoparticle clustering and structuring [25-27]. The exact mechanism of thermal conductivity enhancement of NEILs is unclear. One of the important things is interaction energies of IL with nanoparticles; A. Podgorsek et al. [28] found stronger interactions of ruthenium nanoparticles (RuNPs) with longer alkyl chain ILs by analyzing titration calorimetry and molecular simulation. Those interactions of ILs to the nanoparticles surface may change the surface properties and helps to make cluster of nanoparticles and resulting in enhanced thermal conductivity.

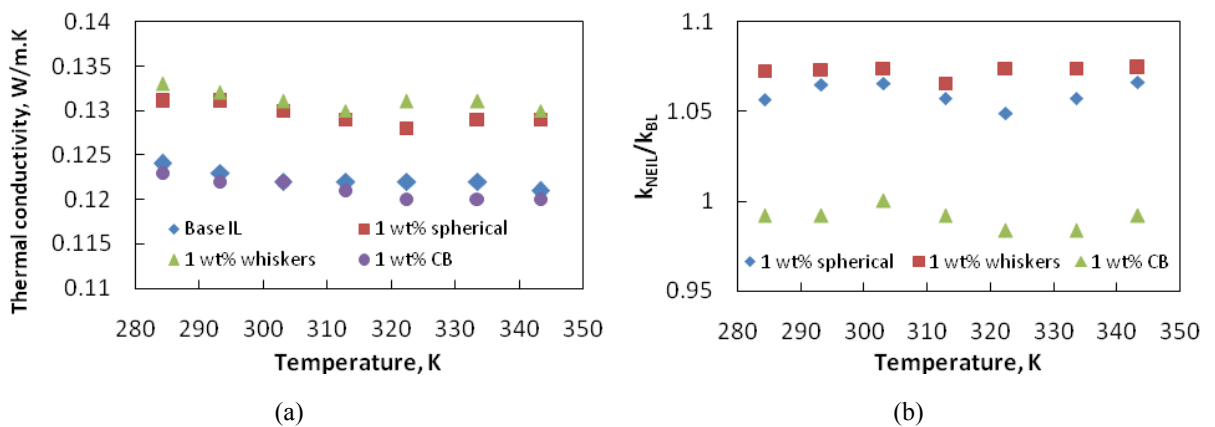


Fig. 5. (a) Thermal Conductivity of base IL and NEILs; (b) normalized thermal conductivity as a function of temperature

## 4. Conclusions

Thermophysical properties such as density, rheological behavior, and thermal conductivity of N-butyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide ( $[\text{N}_{4111}][\text{NTf}_2]$ ) IL and 1 wt%  $\text{Al}_2\text{O}_3$  nanoparticles (spherical and whiskers) and carbon black are measured experimentally. Density of NEILs shows higher values compare to base IL within the measured temperature range. NEILs shows shear thinning behavior and enhanced viscosity with much higher viscosity of CB NEILs compare to  $\text{Al}_2\text{O}_3$  nanoparticles. Whiskers NEILs shows highest thermal conductivity enhancement which is  $\sim 7\%$ . At high temperature viscosity decreases sharply, which implies that at high temperatures NEILs have enhanced thermal conductivity with very less enhanced viscosity. The findings of the present study will help to develop potential heat transfer fluid for CSP system applications.

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