Experimental Investigation of Natural Convection Heat Transfer of Al_2O_3 Nanoparticle Enhanced Ionic Liquids (NEILs)

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Experimental Investigation of Natural Convection Heat Transfer of Al₂O₃ Nanoparticle Enhanced Ionic Liquids (NEILs)

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ABSTRACT

Experimental investigations were carried out regarding natural convection heat transfer of Nanoparticle Enhanced Ionic Liquids (NEILs) in rectangular enclosures of two different sizes with dimensions length×width×height, 50×50×50mm and 50×50×75mm in heated from below. The NEILs were synthesized by dispersing different wt% (0.5, 1.0, and 2.5) of alumina (Al₂O₃) nanoparticles of two different particle shapes (spherical and whiskers) into N-butyl-N-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl} imide, ([C₄mpyrr][NTf₂]) ionic liquid (IL). Heat transfer related thermophysical properties, i.e. density, viscosity, thermal conductivity, and heat capacity of base IL and NEILs were also measured and reported. The experimental measurement shows enhanced density, thermal conductivity, viscosity, and heat capacity of NEILs compared to the base IL and they increase with the nanoparticle concentration. However natural convection heat transfer coefficient was observed to deteriorate for the NEILs compared to the base IL irrespective of the shapes of the particles and aspect ratio of the enclosure and the deterioration increases with the increase of nanoparticle concentration. Interestingly spherical Al₂O₃ NEILs was observed to affect more adversely compared to the whiskers Al₂O₃ NEILs. The observed degradation of the heat transfer performance of the NEILs could not fully be explained by the change of thermophysical properties, which indicates that other factors may play significant roles in this phenomenon and the possible reasons of the degradation is discussed in this paper.

Keywords: Nanoparticle Enhanced Ionic Liquid (NEILs); Density; Viscosity; Heat Capacity; Thermal Conductivity; Convective Heat Transfer Coefficient; Nusselt number; Rayleigh number.

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NOMENCLATURE

q''	Heat flux	[W/m ²]
V	Voltage	[Volt]
I	Current	[amp]
A	Heating surface area	[m ²]
T	Temperature	[°C]
x	Thickness	[m]
k	Thermal conductivity	[W/m.K]
h	Heat transfer coefficient	[W/m ² .K]
c_p	Heat capacity	[J/g.K]
H	Height of the rectangular cavity	[m]
ΔT	Temperature difference	[K]
g	Gravitational acceleration	[m/s ²]

GREEK SYMBOLS

ϕ	nanoparticles volume fraction	[~]
μ	Dynamic viscosity	[kg/s.m]
β	Volumetric thermal expansion coefficient	[K ⁻¹]
α	Thermal diffusivity	[m ² /s]
ν_f	Kinematic viscosity	[m ² /s]
ρ	Liquid density	[kg/m ³]

SUBSCRIPTS

hf	Inside of hot surface
h	Hot surface
cf	Inside of cold surface
c	Cold surface
$NEIL$	Nanoparticle enhanced ionic liquid
BL	Base liquid
s	Nanoparticle
f	Fluid

1. INTRODUCTION

Nanoparticle enhanced ionic liquids (NEILs) have gained attention as a heat transfer fluid (HTF) for solar collector applications, which is formulated by dispersion of small amount of nanoparticles in the base ionic liquids (ILs). The base ILs are organic salts which have low melting points (below 100°C), that are already considered as a potential candidate of HTF for solar collectors and potential replacement of several organic solvents in chemical industry for reaction and separation systems [1-4]. The great interest of ILs are due to 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 [5-8].

There are several research groups working on the thermophysical properties of the ILs based nanofluids. A. Wittmar et al. [9] have studied the rheological behavior of SiO₂ nanoparticles in hydrophobic and hydrophilic imidazolium-based ILs and reported strong effects of ILs hydrophilicity, nanoparticles surface, concentration of the nanoparticles, and temperature on rheological behavior; and improved colloidal stability of nanofluids containing SiO₂ nanoparticles with hydrophobic ILs. N. J. Bridges et al. [10] have studied the heat capacity and thermal stability of NEILs made of 1-Butyl-2,3-dimethylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([C₄mim][NTf₂]) with Al₂O₃ and carbon black (CB) nanoparticles; they have reported higher heat capacity values for Al₂O₃ NEILs and lower heat capacity of CB NEILs. K. Ueno et al. [11-12] studied colloidal stability and viscoelastic properties of nanofluids containing 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl) amide ([C₂mim][NTf₂]) IL [11] and [BF₄] anion-based ILs [12] with silica nanoparticles. B. Wang et al. [13-15] studied the thermal conductivity, rheological and tribological behavior of 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) IL based nanofluids with different size gold nanoparticle [13], gold nanoparticles with different stabilizing agents [14], and functionalized MWCNTs [15]; they reported enhanced thermal conductivity, shear thinning behavior and favorable friction-reduction properties of nanofluids compared to base IL. T. C. Paul et al. [16] have recently reported ~6% enhancement of thermal conductivity of NEILs containing 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([C₄mim][NTf₂]) IL and 1 wt% Al₂O₃ nanoparticles.

Natural convection heat transfer behavior is a fundamental study of any HTF, which has wide engineering and industrial applications, i.e. solar energy collection system, geophysics,

electronic cooling, thermal storage system, and nuclear energy [17]. There are few experimental natural convection studies of water based nanofluids [18-22]. N. Putra et al. [18] experimentally studied the natural convection of Al_2O_3 and CuO-water nanofluids and reported systematic degradation of natural convection heat transfer. D. Wen et al. [19] performed both transient and steady state natural convection experiments of TiO_2 -water nanofluids and they found lower heat transfer coefficient of nanofluids compared to the base fluid. A. G. A. Nnanna [20] investigated natural convection of Al_2O_3 -water nanofluids in the differentially heated enclosure and reported that at concentration $>2\%$, the natural convection heat transfer degrades due to the higher kinematic viscosity of nanofluids. C. H. Li et al. and C.J. Ho et al. [21-22] studied the natural convection of Al_2O_3 nanofluids in cylindrical and square enclosure respectively; they also reported decreased natural convection heat transfer coefficient. All of the previous studies consider water based nanofluids and most of the previous research on ILs based nanofluids are mainly emphasized on the thermophysical properties and thermal stability; none of these studies report the natural convection heat transfer behavior of NEILs. This motivates the authors to study natural convection heat transfer of NEILs.

In the present paper, natural convection experiments were carried out in rectangular enclosures (aspect ratio=height/width= 1 and 1.5) filled with NEILs made of N-butyl-N-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl} imide, ($[\text{C}_4\text{mpyrr}][\text{NTf}_2]$) IL and Al_2O_3 (spherical and whiskers shape) nanoparticles in heated form below. Heat transfer coefficient was calculated by measuring the top and bottom wall temperature and the applied power. For greater fidelity of the reported results, thermophysical properties such as density, viscosity, heat capacity, and thermal conductivity of the NEILs were also measured and reported.

2. EXPERIMENTAL METHODS

2.1. Material and Synthesis of NEILs

The 0.5%, 1.0%, and 2.5% (weight %) NEILs were prepared by N-butyl-N-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl} imide, ($[\text{C}_4\text{mpyrr}][\text{NTf}_2]$) IL with Al_2O_3 (spherical and whiskers shape) nanoparticles. 99% pure $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ IL was purchased from IoLiTec Company (Germany). The chemical structure (Fig.1) of the anion, cation, and the molecular formula of the IL are as follows:

Molecular formula: $C_{11}H_{20}F_6N_2O_4S_2$

Al_2O_3 nanoparticles were purchased from Sigma-Aldrich, USA. Spherical shape nanoparticles are γ -phase with particle size <50 nm (TEM) and surface area >40 m²/g (BET); whiskers nanoparticles having diam. $\times$ L, 2-6 nm $\times$ 200-400 nm and aspect ratio > 100 (TEM). Al_2O_3 nanoparticles was dispersed in the base IL by using vortex mixture. NEILs were processed for around 90 min in the vortex mixture to break possible aggregations of nanoparticles.

2.2. Thermophysical property measurements

The density of base IL and NEILs was measured by a Pycnometer (Thomas Scientific). The Pycnometer was 1 mL in size. The empty Pycnometer and sample filled Pycnometer was weighing by using METTLER TOLEDO balance which has a precision of 0.01 mg. Density was determined by those weight difference. The Pycnometer and the samples were placed in a thermal bath (Thermo NESLAB) to maintain a uniform temperature. Before using for nanofluids the Pycnometer was calibrated with water. The volume expansion coefficient was calculated by using the equation

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (1)$$

Viscosity of the base IL and NEILs was 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 1 mL. 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 by using standard oil.

Thermal conductivity of the base IL and NEILs was measured using KD2 Pro thermal property analyzer (Decagon Device, USA). The measurement 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 $\pm 0.01\text{K}$.

The heat capacity of IL and NEILs was measured using Differential Scanning Calorimetry (DSC Q2000 from TA instruments Inc.). The sample was placed in a standard aluminum hermetic pan covered with lid and the average sample size was 13.58mg. Nitrogen was used as cooling system at flow rate of 40 mL/min. The DSC run was performed from 25°C to 340°C at a heating rate of 10°C/min.

2.3 Measurement of heat transfer coefficient

2.3.1. Experimental System

Fig. 2(a) shows the schematic of the rectangular enclosure used in the experimental investigations; Fig. 2(b) is the photograph of experimental setup, which includes test enclosure, heater, insulation, thermal bath, flow meter, power supply, data acquisition system, and thermocouples. The experimental test sections are rectangular enclosure, made with clear polycarbonate Lexan sheet and the dimensions are (length×width×height) 50×50×50mm and 50×50×75mm.

Two ends of the enclosure are made with conductive copper plates of thickness 3 mm to perform as hot and cold surfaces. There are two openings in the top copper sheet which are for filling liquid and removing air bubbles from the enclosure. The top copper sheet is maintained at a uniform temperature by flowing cold water through a secondary enclosure of 25 mm height situated on top of the copper sheet. A flexible silicone rubber fiberglass insulated heater (20W, from OMEGA) is closely attached to the lower copper surface. The heating power is supplied from a DC power supply (30W, E3612A, from Agilent Inc). The heating and cooling surface temperatures are measured by using K-type thermocouples of 0.13 mm diameter. There are two other thermocouples which are connected to the cold water inlet and outlet lines to measure the inlet and outlet temperatures of the cold water. All of the thermocouples are calibrated using a constant temperature bath (Thermo NESLAB) and thermocouples are connected to the data acquisition system by Labview software. All of the thermocouples are connected to a National Instrument (NI) data acquisition system cDAQ 9178 via a temperature card NI 9211 which was interfaced with a computer. Labview software was used for collecting and recording the data.

The input voltage and current were measured from the display of the power supply. The whole system was insulated with the fiberglass insulation to reduce the heat loss to the environment.

2.3.2. Data processing

Before performing any experiment the test enclosure was rinsed thoroughly several times with DI-water and the liquid was poured into the test enclosure with care to avoid entrapment of any air bubbles into the enclosure. The NEILs was shaken very well before filled into the enclosure. After preparing the test section, turn on the power supply and set the desired voltage. During the experiment the hot and cold surface temperatures were monitored and recorded until a steady state was reached. After recording the data, the voltage increases to the next desired value. In the experiment different Rayleigh numbers have been achieved by changing the heat flux. Heat flux q'' was calculated from the input power of the heater and dividing by the surface area of the copper plate.

$$q'' = \frac{VI}{A} \quad (2)$$

where V is the input voltage, I is the input current, A is the surface area of the heater. Considering the heat loss, corrected heat flux (q''_{corr}) was calculated from the heat removed by the cold water and actual input heat. Hot surface temperature, T_{hf} and cold surface temperature, T_{cf} of the internal surface have been calculated from the thermocouple readings and using the one dimensional (1-D) steady state heat conduction equation:

$$T_{hf} = T_h - \left(\frac{q''_{corr}}{k_c} x \right) \quad (3a)$$

$$T_{cf} = T_c + \left(\frac{q''_{corr}}{k_c} x \right) \quad (3b)$$

Finally the heat transfer coefficient h was calculated by:

$$h = \frac{q''_{corr}}{(T_{hf} - T_{cf})} \quad (4)$$

2.3.3. Experimental Uncertainty

The measurement uncertainty of thermocouples, voltage, and current are $\pm 0.2^\circ\text{C}$, $\pm 0.1\text{V}$, and $\pm 0.001\text{A}$. A systematic uncertainty analysis was performed using standard Kline and McClintock method [23].

$$W_p = \sqrt{\sum_{i=1}^n \left(\frac{\partial p}{\partial a_i} w_i \right)^2} \quad (5)$$

where, W_p is the total uncertainty of calculated parameter, p , and a_i variables of functional dependence, and w_i is the uncertainty of the independent variables. Input power uncertainty was estimated as $\pm 1.57\%$, heat transfer coefficient has an uncertainty of $\pm 2.23\%$. Since the dimensionless numbers are the functions of numerous measured quantities and physical properties, therefore the uncertainty will propagate. The maximum uncertainties associated with the Nusselt number and Rayleigh number were calculated as $\pm 4.59\%$ and $\pm 11.58\%$ respectively.

3. RESULTS AND DISCUSSION

3.1. Density of NEILs

The density of different spherical Al_2O_3 concentration NEILs as a function of volume fraction and temperature are presented in Fig. 3(a) and 3(b) respectively. The density of base IL and NEILs decreases with temperature within the measured temperature 283-343K. It is clear that the NEILs has higher density compared to the base IL because of high density Al_2O_3 nanoparticles. The experimental measurements were compared with the calculated effective density using the mixing theory [22] and it is clear that experimental measurements matches well with the theoretical calculation.

$$\rho_{NEIL} = \phi \rho_s + (1 - \phi) \rho_{BL} \quad (6)$$

Fig. 3(c) presents the density of NEILs with Al_2O_3 whiskers as a function of temperature; these density data were used for natural convection heat transfer parameter calculations. No variations were observed in the density data for different shape of particles.

3.2. Viscosity of NEILs

The effective dynamic viscosity of NEILs as a function of the nanoparticles volume fraction of two different shapes is presented in Fig. 4(a). The measured effective dynamic viscosity of NEILs is also compared with Batchelor equation [24] for dilute non-interacting suspensions of spherical particles.

$$\frac{\mu_{NEIL}}{\mu_{BL}} = 6.2\phi^2 + 2.5\phi + 1 \quad (7)$$

where μ_{NEIL} and μ_{BL} are the viscosity of NEIL and base liquid, ϕ is the nanoparticle volume fraction. The relative shear viscosity increases with nanoparticle concentration and enhancement is non-linear. It can be seen from the Fig. 4(a) that the model could not predict the effective viscosity of NEILs. The higher viscosity indicates the strong particle-particle interactions of NEILs. Predicted results were found to be lower compared to the measured values as the model does not take into account nanoparticles clustering which is very common for the NEILs. The similar enhancement of viscosity of NEILs was also observed by E. B. Fox et al. [25], N. J. Bridges et al. [10], K. Ueno et al. [11], and B. Wang et al. [13] for ILs containing Al_2O_3 , SiO_2 , and Gold (Au) nanoparticles. From Fig. 4(a), it can also be seen that the effective viscosity of spherical nanoparticles NEILs shows higher values compared to that of whiskers nanoparticles NEILs which contradict with previous study of conventional water- Al_2O_3 nanofluids with different shape of nanoparticles by E. V. Timofeeva et al. [26]. They 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. But the same higher viscosity of NEILs with spherical nanoparticles compare to whiskers nanoparticles was reported by E. B. Fox et al. [25], where they have presented optical micrograph of NEILs and have seen that the whiskers particle cluster diameter was smaller than the spherical particles. Fig. 4(b) and (c) represents the viscosity of spherical and whiskers NEILs as a function of temperature respectively. It can be seen that the effective viscosity of NEILs shows higher values compare to the base IL and it increases with the concentration of nanoparticles over the measured temperature range. Also shows highly temperature dependency of NEILs as decreasing viscosity with increasing temperature.

3.3. Thermal conductivity of NEILs

The effective thermal conductivity of NEILs as a function of nanoparticle concentration along with existing equations [22, 27] is presented in Fig. 5(a), where thermal conductivity of NEILs is normalized with respect to the corresponding thermal conductivity of base IL. The compared correlations are:

$$\text{Maxwell equation: } \frac{k_{NEIL}}{k_{BL}} = \frac{k_s + 2k_{BL} - 2\phi(k_{BL} - k_s)}{k_s + 2k_{BL} + \phi(k_{BL} - k_s)} \quad (8)$$

$$\frac{k_{NEIL}}{k_{BL}} = 1 + 2.944\phi + 19.672\phi^2 \quad (9)$$

where K_{NEIL} , K_{BL} , $k_n = 36 \text{ W/mK}$ are the thermal conductivity of NEIL, base IL, and Al_2O_3 nanoparticles respectively. Φ is the nanoparticle volume fraction. It is clear from the Fig. 5(a) that the thermal conductivity increases with the wt% of nanoparticles and the maximum enhancement was observed ~9% and ~13% for 2.5 wt% of spherical and whiskers NEILs respectively. As of Fig. 5(a) the enhancement of thermal conductivity of NEILs by using Maxwell model and equ.(9) shows lower than that of experimentally measured value. May be same as viscosity, the model only considers the thermal conductivity of particles, base liquid, and nanoparticle volume fraction. But our predicted and experimental results are consistent with previously published literature [14, 25] where they use, gold and Al_2O_3 nanoparticles with different base ILs. From the Fig. 5(a) it is also clear that thermal conductivity enhancement of whiskers nanoparticles is always higher than the spherical nanoparticles. It is noted by E. V. Timofeeva et al. [26] that increasing the particle aspect ratio has a positive effect on the thermal conductivity enhancement. In Fig. 5(b) and (c) presents the effective thermal conductivity of spherical and whiskers NEILs respectively as a function of temperature. In both NEILs the enhancement shows little effect of temperature.

3.4. Heat capacity of NEILs

The heat capacity of base IL and spherical and whiskers NEILs over 25-345°C with an interval of 10°C are presented in Fig. 6(a) and (b) respectively. It is clear from the Fig. 6 that the heat capacity of NEILs is much higher than the base IL over the measured temperature range and heat capacity increases almost linearly with temperature. Measured heat capacities of NEILs

were compared with the existing classical theoretical model of heat capacity for a mixture where base IL and nanoparticles are assumed at thermal equilibrium [28]:

$$C_{p,NEIL} = \frac{\phi_s \rho_s C_{p,s} + \phi_{BL} \rho_{BL} C_{p,BL}}{\phi_s \rho_s + \phi_{BL} \rho_{BL}} \quad (10)$$

where, $C_{p,NEIL}$, $C_{p,s} = 0.791 \text{ J/g.K}$, and $C_{p,BL}$ are the heat capacity of NEILs, nanoparticles, and base IL respectively, ϕ is the nanoparticles volume fraction. ρ_s and ρ_{BL} are the density of nanoparticles and base IL respectively. The predicted heat capacity of NEILs based on the equation shows slightly lower value than the base IL but the experimental measured heat capacity of NEILs shows much higher value compared to the base IL. That means, the significant enhancement of heat capacity of NEILs cannot be predicted by the model and more sophisticated investigations will be required to explain these enhancements. Meanwhile, similar enhancement of heat capacity with a small amount of Al_2O_3 nanoparticles with $[\text{C}_4\text{mmim}][\text{NTf}_2]$ IL was observed earlier by N. J. Bridges et al. [10].

3.5. Natural convection heat transfer coefficient

3.5.1. Heat transfer experiments with DI-water

Natural convection in the rectangular cavity heated from below does not depend on the critical temperature difference between the top and bottom surface. The condition of heated from below can be expressed in terms of the critical Rayleigh number which is an important dimensionless parameter in natural convection, and is defined as the ratio of the buoyancy force to the viscous force acting on the fluid. Natural convection in the rectangular cavity heated from below occurs once the Rayleigh number exits the critical value $Ra > 1708$ [29].

Initially the experiment was carried out with DI-water and the results have been compared with the other published results [18-19, 21] to ensure the credibility of the experimental setup and procedure. Nusselt number (Nu) as a function of the Rayleigh number (Ra) for DI-water was compared with that of the published results which is presented in our previous publication [30]. The Nusselt and the Rayleigh number are computed by the following equations:

$$Nu = \frac{hH}{k_f} \quad Pr = \frac{\nu_f}{\alpha} \quad Gr = \frac{g\beta\Delta TH^3}{\nu_f^2} \quad (11)$$

$$Ra = Gr.Pr \quad (12)$$

where, H is the height of the enclosure, k_f is the thermal conductivity, Pr is the Prandtl number, ν_f is the kinematic viscosity, $\alpha(= \frac{k_f}{\rho C_p})$ is the thermal diffusivity, Gr is the Grashof number, β is the volume expansion coefficient, ρ is the density, C_p is the heat capacity of fluid, ΔT is the temperature difference between hot and cold surface fluid, and g is the gravitational acceleration. All the fluid properties were evaluated at the average ($T_{av} = \frac{T_{heated} + T_{cooled}}{2}$) of the heated and the cooled surface temperature. The natural convection correlation can be represented as,

$$Nu = cRa^n \quad (13)$$

where c and n are the empirical constants.

3.5.2. Heat transfer behavior of NEILs

After having confidence with the experimental facilities for DI-water, the systematic natural convection experiments were performed for $[C_4mpyrr][NTf_2]$ base IL and different concentration of spherical and whiskers Al_2O_3 NEILs at two different aspect ratios (AR-1 and 1.5). The initial transient heating and cooling surface temperature of base IL and spherical Al_2O_3 NEILs for AR-1 is presented in Fig. 7. It is clear from the Fig. 7 that 2.5 wt% NEILs have the highest and the base IL have the lowest heating surface temperature. Also, it takes a longer time to reach the steady state for 2.5 wt% NEILs. The steady state temperature difference between heating and cooling surfaces was increased with nanoparticles concentration which results in the systematically decreased heat transfer coefficient. The scenario occurred in both aspect ratios enclosures.

Effective Rayleigh number for the same temperature difference of three concentrations of spherical Al_2O_3 NEILs have presented in Fig. 8, where the Rayleigh number was normalized by effective Rayleigh number of NEILs divided by the Rayleigh number of base IL. The effective Rayleigh number of NEILs was calculated using the corresponding effective thermophysical properties of NEILs. The Fig. 8 shows that the normalized Rayleigh number decreased with nanoparticle concentration. This means increasing nanoparticle concentration increases the

viscous force in the rectangular cavity, which results in the reduction of Rayleigh number as well as natural convection heat transfer coefficient.

The Nusselt number and Rayleigh number (both AR-1 and 1.5) of base IL and the different concentration of spherical and whiskers NEILs are presented in Fig. 9(a) and (b) respectively. It is clear from the Fig. 10 that Nusselt number of both NEILs shows lower value compared to the base IL over the measured Rayleigh number range. Both AR shows at almost the same rate of degradation. Fig. 10(a) and 10(b) represents the comparison of natural convection heat transfer results of spherical and whiskers Al_2O_3 NEILs for AR-1 and 1.5 respectively. In both aspect ratios it is clear that whiskers Al_2O_3 NEILs shows higher Nusselt number compared to spherical Al_2O_3 NEILs at the same Rayleigh number. The higher heat transfer of whiskers NEILs may be the consequence of the higher effective thermal conductivity (Fig. 5(a)) and lower effective viscosity (Fig. 4(a)) of whiskers NEILs compared to the spherical NEILs. The same higher heat transfer performance of cylindrical shape nanoparticles was found analytically in shell and tube heat exchanger [31] and experimentally in the oscillating heat pipe [32]. The percentage of degradation of heat transfer coefficient is clear in Fig. 11 where heat transfer coefficient of spherical NEILs are normalized by base IL is plotted as a function of temperature difference.

It is generally thought that the change of effective thermophysical properties has a great influence on the degradation of the natural convection performance of nanoparticle enhanced fluids [22, 33]. Fig. 12 was constructed by all of the effective thermophysical properties and effective heat transfer coefficient of spherical NEILs to understand and quantify the degree with which thermophysical properties effects much, there are also other factors with the thermophysical properties that lead to degradation of the natural convection of NEILs. In the natural convection correlation equ.(13), the Nusselt number and Rayleigh number are presented and forms equ. (14):

$$Nu = cRa^n$$

$$\frac{hH}{k_f} = c \left(\frac{g\beta\Delta TH^3 c_p \rho^2}{\mu k_f} \right)^n \quad (14)$$

From the equ.(14) normalizing the heat transfer coefficient by dividing the heat transfer coefficient of NEILs to IL we can find the correlation:

$$\frac{h_{NEIL}}{h_{BL}} \sim \left(\frac{\beta_{NEIL}}{\beta_{BL}}\right)^n \left(\frac{\rho_{NEIL}}{\rho_{BL}}\right)^{2n} \left(\frac{C_{p,NEIL}}{C_{p,BL}}\right)^n \left(\frac{\mu_{NEIL}}{\mu_{BL}}\right)^{-n} \left(\frac{k_{NEIL}}{k_{BL}}\right)^{1-n} \quad (15)$$

From the Fig.12 and previous thermophysical properties (Fig. 3-6) it can be seen that all of the thermophysical properties increases with nanoparticle concentration. In the normalized heat transfer coefficient correlation, all of the thermophysical properties except dynamic viscosity have the negative impact on heat transfer coefficient. In the correlation, inserting a typical natural convection correlation exponent value of $n = 1/3$, the normalized heat transfer coefficient was calculated and presented in Fig.12. Although all properties are enhanced with nanoparticle concentration and have a positive effect except dynamic viscosity, heat transfer coefficient decreases with nanoparticle concentration, and the highest degradation was ~22% for 2.5 wt% NEILs. That means the negative effect of enhanced viscosity surpassed the enhancement of other thermophysical properties. However, experimentally the maximum degradation was ~68% (as of Fig.11) for 2.5 wt% NEILs which indicates the change of thermophysical properties could not fully explain the experimental degradation of natural convection performance of NEILs. But no matter the amount of percentage decrease, still due to effective thermophysical properties of NEILs degrade the natural convection heat transfer coefficient as of Fig. 12. The present observations of natural convection behavior of NEILs are consistent with the previous experimental studies of the water based nanofluids [18-22]. There are several explanations of the deteriorating behavior of water based nanofluids mentioned by previous researchers. N. Putra et al. [18] emphasizes the role of particle fluid interaction and nanoparticles sedimentation as possible reasons for this deterioration and along with those D. Wen et al. [19] included the thermophysical properties influence, convection by concentration difference, influence of P^H , and particle-surface interaction. C.J. Ho et al. [21] added that particles-fluids interactions and transport mechanisms as similar to Brownian diffusion at high temperature difference.

In addition to the above mentioned factors, deterioration of natural convection heat transfer of NEILs may have other influences. One of the important things is interaction energies of IL with nanoparticles; A. Podgorsek et al. [34] found stronger interactions of ruthenium

nanoparticles (RuNPs) with longer alkyl chain ILs by analyzing titration calorimetry and molecular simulation. W. R. Carper et al. [35] also reported interactions of ILs with Al_2O_3 and reveals that ILs makes a protective coating on the nanoparticle surface which helps to better the tribological properties. A. S. Pensado et al. [36] also performed the molecular dynamic (MD) simulations of 2 nm RuNPs in ILs to see the solvation and stabilization of nanoparticles and found good contact with nanoparticles and anion and cation of ILs with nanoparticles solvated preferentially by the charged group of the IL ions. Those interactions of ILs with the nanoparticles surface may change the surface properties and helps to make cluster of nanoparticles. Such clustering is prominent to agglomeration and sedimentation formation which make extra resistance to flowing heat to the NEILs. So the plausible mechanisms of degradation of NEILs are combinations of effect of thermophysical properties, particle-fluid interaction and clustering of nanoparticles which influences the formation of sedimentation. However, extensive theoretical and experimental studies are required to explain the exact cause.

4. CONCLUSIONS

In the present study, we for the first time experimentally investigate the natural convection behavior of Nanoparticle Enhanced Ionic Liquid (NEILs) formulating with spherical and whiskers Al_2O_3 nanoparticles into N-butyl-N-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl} imide, $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ ionic liquid. The thermophysical properties such as density, viscosity, thermal conductivity, and heat capacity also measured experimentally. From the experimental results the following conclusions can be drawn:

- All of the thermophysical properties increase with nanoparticles concentration. The measured effective density of NEILs correlates well with the calculated data by mixing theory. Viscosity of NEILs is highly temperature dependent and higher than the base IL. The enhancement also depends on the shape of the particles. The theoretical effective viscosity model underpredict the experimental measurements. The thermal conductivity of the NEILs is enhanced by ~9 and ~13% for 2.5wt% nanoparticles loading of spherical and whiskers nanoparticles respectively. The measured thermal conductivity of NEILs shows higher values than those predicted by Maxwell's model within the investigated temperature range. Heat capacity of NEILs enhanced by ~62% and ~45% for 2.5wt% nanoparticles loading of spherical and whiskers nanoparticles respectively.

-The systematic degradation of natural convection heat transfer of both spherical and whiskers NEILs was observed for both aspect ratios. The whiskers NEILs had slightly higher heat transfer coefficient compared to the spherical NEILs. The relative change of effective thermophysical properties are not fully responsible for the degradation of the natural convection of NEILs. In addition to thermophysical properties, particle-fluid interaction and clustering of nanoparticles also play a role in degrading the natural convection heat transfer.

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Figure 1:

Cation

Anion

Figure 2:

(a)

(b)

Figure 3:

(c)

Figure 4:

(a)

(b)

(c)

Figure 5:

(a)

(b)

(c)

Figure 6:

(a)

(b)

Figure 7:

Figure 8:

Figure 9:

(a)

(b)

Figure 10:

(a)

(b)

Figure 11:

Figure 12: