Evaluation of stability and viscosity of [C$_2$mim][DCA] based ionanocolloids

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Abstract. In the search for the optimization of heat transfer systems, Ionanocolloids (INCs) as we have termed here, have revealed as very attractive choices due to their increasingly potential applications in thermal energy areas. By definition, INCs are suspensions of nanoparticles (NPs) into Ionic Liquids (ILs). Besides a high degree of versatility and enhanced thermal properties, these new class of fluids are considered as green solvents due to their negligible vapor pressure, non-flammability and recyclability. Despite the great advantages of using these INCs, their industrial application is still a challenge due to low stability and high viscosity issues attributed to them. In this work, different Ionanocolloids were prepared by two-step method, using 1-ethyl-3-methylimidazolium dicyanamide ([C$_2$mim][DCA]) together with deionized water as base fluids and 3 different NPs: Titanium(IV) Oxide, Silicon Oxide and Aluminum Oxide. The stability and viscosity of these mixtures were then evaluated and the results are reported.

1. Introduction
As the push for greener energy alternatives intensifies, due to the ever present problem of climate change, all types of technology have had to undergo some scale of adaptation to these pressing concerns, such as with the change from Chlorofluorocarbons (CFCs) to less harmful options in refrigeration systems in the late 20$^{th}$ and early 21$^{st}$ century. ILs have garnered increased attention in the area of heat transfer systems as a green alternative to currently used commercial fluids, from both scientists and industry experts alike, thanks to their categorization as a green solvent and great features such as high thermal stability, high ionic conductivity, negligible vapor pressure, non-flammability and recyclability [1].

ILs have a wide array of applications such as use in batteries, solar panels, fuel cells, lubricants and etc. in thermal energy areas [1], and are used as base fluids for the dispersion of NPs to be applied as heat transfer fluids (HTFs). These INCs are reported to possess enhanced thermophysical properties compared to conventional fluids, as well as base ILs. For that purpose, a wide variety of NPs have been used, such as Single and Multi-Walled Carbon Nanotubes, Copper Oxide, Aluminum Oxide, Silicon Oxide, Titanium Oxide and many more, and have indeed been shown to enhance some of the mentioned properties as reviewed by [2].

Some of the challenges that these fluids present are, on one hand, due to their rheological properties, namely their high viscosity at low temperatures and non-Newtonian behaviour [3][4][5] when compared to not only their base ILs, but also when compared with commercial HTFs which, in turn, will require more mechanical energy from the system to offset the extra pumping power.
necessary to maintain flow conditions. On the other hand, the difficulty in stabilizing the INCs is another critical point for this class of fluids. Some approaches to enhance long-term stability of these fluids, like addition of surfactants, functionalization of NPs surface, and pH changing of the solution are reported by researchers [2][6]. However, they may influence the reliability of the effective thermal conductivity measured and can additionally cause corrosion, produce foam and are known to degrade at high temperatures [2][6].

This work focused on the preparation and stabilization of INCs using 1-ethyl-3-methylimidazolium dicyanamide ([C₂₃mim][DCA]) IL and 3 different types of NPs, Titanium(IV) Oxide (TiO₂), Silicon Oxide (SiO₂) and Aluminum Oxide (Al₂O₃), together with the analysis of the viscosity of the stable dispersions. Our ultimate goal was to achieve a stable and pure mixture as much as possible (without surfactant addition), taking into account the use of mixtures with deionized water and ionic liquids as base fluids to also reduce overall costs of INCs, since they are still economically disadvantageous when compared to the commercially available HTFs.

2. Materials and Methods

For the presented work, the following materials were used: Ionic Liquid 1-Ethyl-3-methylimidazolium dicyanamide (98 % purity) (Iolitec GmbH, Germany), Silicon oxide powder (non-porous), (20 nm, 99.5 % purity) (Iolitec GmbH, Germany), Titanium(IV) oxide powder, anatase, (20 nm, 99.5 % purity) (Iolitec GmbH, Germany), Aluminum oxide, (40 – 50 nm, 99.5 % purity) (Alfa Aesar by ThermoFisher GmbH, Germany) and deionized water (18 MΩ cm⁻¹, Milli-Q system).

To prepare INC samples, the following two-step method was applied: The base fluids were prepared with different mass fractions of ILs to deionized water, ranging from 10 – 75 wt.%. The mixtures were magnetically stirred for 1 hour and were followed by the weighing and addition of the desired masses of nanoparticles, in the range of 0.01 – 0.1 wt.%. This mixture was then taken to the ultrasonic homogenizer (Hielscher UP200Ht) for 1 hour and stored in glass vials to be further analysed.

The viscosity was measured using Brookfield Ametek DVNext Rheometer, with ±1.0 % of range accuracy, that required a volume of 0.5 cm³ of sample fluid. Fluid was at room temperature (294 K), and a minimum of 3 readings were taken per concentration of nanoparticle 0 – 0.1 wt.%, which in this case was Silicon Oxide. The variation between measurements was smaller than 5 %. In addition, two extra analysis were performed: on an INC with 75 % of IL and 0.02 wt.% SiO₂, and the pure IL to have a better understanding of the behaviour of the viscosity when the IL is mixed with deionized water.

3. Results and Discussion

3.1. Stability Evaluation

INCs prepared with both TiO₂ and Al₂O₃ failed to stabilize, becoming fully precipitated after 24 hours as can be seen in Figures 1 and 2. It is expected that the use of ionic liquids as base fluids will improve stability of INCs, due to the formation of a electrostatic layer of the ions from the solution on the surface of the NPs. However, with the use of small ratios of ILs:deionized water the attractive Van der Walls forces between NPs might be significant and hence, the clustering followed by precipitation of them was observed [2]. Thus, these two INCs are not further studied.

On the other hand, mixtures with SiO₂ became increasingly stable with the increase of IL concentration, reaching perfect stability with concentrations above 50 % IL, which can be seen in Figure 3 having the suspensions been stable for more than one month.

3.2. Viscosity

The analysis started by measuring the viscosity of water and obtained the value of 0.97 (±0.05) mPa·s at a room temperature (294 K) which is consistent with tabulated values throughout
Figure 1. 10 % IL with 0.02 % TiO₂ at preparation(left) and after 24 hours(right)

Figure 2. 10 %, 20 % and 30 % IL with 0.02 % Al₂O₃ at preparation(top) and after 24 hours(bottom)

Figure 3. 50 % IL with, from left to right, 0 %, 0.01 %, 0.02 %, 0.03 %, 0.04 %, 0.05 % and 0.1 % SiO₂.

the literature. Then, the pure ionic liquid was evaluated and the value of 14.91 (±0.2) mPa · s was obtained, which is in accordance with values given by [7]. Viscosity analysis of the INC with 50 % concentration of IL and different concentrations of SiO₂ is presented in Figure 4.

Figure 4. Viscosity of 50 % IL with SiO₂.
It is clear from Figure 4 that the addition of NPs increases viscosity. For instance, the dispersion of 0.01% of NPs promoted an increase in viscosity of around 7.2% in relation to the viscosity of the base fluid. Moreover, the viscosity of the INC with 0.1% concentration of NPs did not follow the trend of previous fluids.

Measurements performed on the INC with 75% of IL resulted in a value of 4.90 (±0.02) mPa·s which, when compared to the INC with 50% of IL with the same concentration of NPs (0.02%), shows an increase of around 111%. Regarding the viscosity of the pure IL, it has viscosity of around 204% higher than the INC with 75% of IL and 543% higher than the INC with 50% of IL. These results are reflective of the complexity of INCs, and show the high impact of NPs addition into ionic liquids. Such influence may result in the modification of the fluids flow to a non-Newtonian behaviour and this phenomenon is ascribed to the increase of the interactions between the nanoparticles as concentration increases, which results in the transition of ordering and disordering state of the molecules [5].

4. Conclusion
This work evaluated the stability and viscosity of INCs with different ratios of IL/deionized water as base fluids and different NPs concentrations. One of the biggest concerns of the industrial applications of INCs as heat transfer fluids refers to their stability, which can be achieved by combining different concentrations of SiO\textsubscript{2} nanoparticles with a base fluid containing deionized water and 50% of IL. Another limitation of INCs use in large-scale is their high costs associated with the initial cost of ILs, which is reduced by using mixtures with deionized water, that also has the added benefit of reducing viscosity drastically, and hence the pumping power demanded for the operation of thermal systems. While extensive studies have recently emerged from researchers on the properties of INCs, there is still much to be done in investigating applications of these fluids in greater detail and by overcoming challenges like cost, stability and viscosity. Nevertheless, the never-stopping development in this area indicates that INCs have enormous potential to be considered as heat transfer fluids for large-scale applications in the near future.

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