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Thermodynamic properties and thermal stability of ionic liquid-based nanofluids containing graphene as advanced heat transfer fluids for medium-to-high-temperature applications

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ABSTRACT

Here the experimental technique for measuring the thermal conductivity of nanofluids at the temperatures above 100 °C has been developed, and a systematic research on the thermodynamic properties including thermal conductivity, viscosity, specific heat and density, of the graphene-dispersed nanofluids based on the ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF_4), has been conducted at the temperatures ranging from room temperature to around 200 °C. The thermal conductivity of the nanofluid containing graphene of as low as 0.06 wt% increases by 15.2%–22.9% as the tested temperature varies from 25 to 200 °C, as compared with that of the base fluid. The viscosity of [HMIM]BF_4 and its graphene-dispersed nanofluids dramatically decreases to 6.3 cp with the temperature increasing to 210 °C, which just favors their medium-to-high-temperature applications. The specific heat and density of the graphene-dispersed nanofluids exhibit a slight decrease as compared with those of [HMIM]BF_4. It is found that the thermodynamic properties of [HMIM]BF_4 and its GE-dispersed nanofluids are superior to those of the commercial heat transfer fluid Therminol VP-1. The thermogravimetric analysis shows that the initial decomposition temperature of the GE-dispersed nanofluids is very close to 440.6 °C of [HMIM]BF_4, indicating that all of them possess good thermal stability. This novel class of fluids based on the ionic liquid shows great potential for use as advanced heat transfer fluids in medium- and high-temperature systems such as solar collectors.

1. Introduction

Solar energy is the most abundant and easily available renewable resource and can be supplied without any environmental pollution. Among all the ways of harnessing the limitless power of the sun, solar energy photothermal conversion and utilization is the most common and convenient one. Being a major component of any solar thermal system, solar collectors absorb the solar radiation, convert it into heat energy, and then transfer the heat through a fluid for useful applications [1]. It is no doubt that the thermodynamic properties including thermal conductivity (TC), specific heat, viscosity and density, of the heat transfer fluid (HTF), take an important role in determining the solar energy utilizing overall efficiency [2,3]. For medium-to-high-temperature solar applications such as solar thermal power, the HTFs with excellent thermodynamic properties as well as good thermal stability are highly desirable.

Incorporation of nanosized solid particles with an HTF to prepare a nanofluid has been proven to be an effective route for improving the thermodynamic properties of the base HTF, especially its TC [4–6]. Thus, nanofluids have attracted extensive attention since the pioneer work by Choi et al., in 1995 [7]. However, most of the previous researches focused on the nanofluids based on the traditional HTFs, such as water, ethyl glycol and the synthetic oil (Therminol VP-1) [8–10]. It is obvious that the nanofluids based on water and ethyl glycol are not suitable for medium-to-high-temperature applications; the synthetic oil suffers from flammability and high vapor pressure at the temperatures above 257 °C, though it has been a kind of commercial HTFs. As a result, it is necessary to develop novel nanofluids based on the fluids other than those traditional fluids for medium-to-high-temperature applications.

Ionic liquids (ILs) are a group of molten salts with a melting point below 100 °C as well as a wide liquid temperature range from

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room temperature to a maximum temperature of 459 °C [11,12]. The studies on the thermophysical properties of some ILs have revealed that ILs have the advantages of high density and heat capacity, good thermal and chemical stability and low vapor pressure [13–17]. These favorable thermophysical properties make ILs show great promise for use as HTFs in medium- and high-temperature heat transfer systems. Recently, aiming at further improving the thermophysical properties of ILs, several nanomaterials including multi-walled carbon nanotubes (MWCNTs) and Au, CuO and Al_2O_3 nanoparticles have been added into some ILs to prepare IL-based nanofluids (Ionanofluids), respectively, and their thermophysical properties have been investigated [18–25]. It has been shown that these Ionanofluids exhibit enhanced TC compared with the corresponding ILs, suggesting that the addition of nanomaterials can overcome the disadvantage of low TC inherent in ILs. However, although the heat capacity of the $[C_4mim][PF_6]$-based Ionanofluids containing MWCNTs have been evaluated at the temperatures between 35 and 150 °C [18] and the density and heat capacity of the $[C_4mmim][NTf_2]$-based Ionanofluid containing Al_2O_3 or carbon black have been measured at 200 °C [26], few investigations on nanofluids have been carried out at the temperatures above 100 °C and involved all their thermodynamic properties including TC, specific heat, viscosity and density. Note that Ionanofluids are developed for use in the medium-to-high-temperature heat transfer systems, different from the nanofluids based on water and ethylene glycol. Therefore, it is of significance to conduct a systematic research on all the thermodynamic properties of novel Ionanofluids at a wide temperature range.

The TC of as high as around 5000 W m^{-1} K^{-1} makes graphene (GE) to be a promising nanoadditive for nanofluids [27,28]. In our previous paper [29], the GE-dispersed Ionanofluids based on 1-hexyl-3-methylimidazolium tetrafluoroborate $(HMIM]BF_4)$ were prepared for the first time without using any surfactant and their thermophysical properties were measured at the temperatures below 100 °C. In the current work, the experimental technique for measuring the TC of nanofluids at the temperatures above 100 °C has been developed for the first time, and the thermodynamic properties including TC, specific heat, viscosity and density, of $[HMIM]BF_4$ and its GE-dispersed Ionanofluids, have been systematically investigated at a temperature range from room temperature to around 200 °C. In addition, the thermal stability of $[HMIM]BF_4$ and its GE-dispersed Ionanofluids has been evaluated, and the feasibility of the GE-dispersed Ionanofluids for use as advanced HTFs in medium- and high-temperature heat transfer systems has been demonstrated.

2. Experimental

2.1. Chemicals and materials

Graphite was purchased from Nanjing XFNano Material Tech Co., Ltd. (China); H_2SO_4, HNO_3, and $KMnO_4$, from Alfa Aesar (Ward hill, MA, USA). $[HMIM]BF_4$ (CAS Number, 244193-50-8) was provided by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

2.2. Preparation of GE-dispersed nanofluids

The procedure for preparing GE from graphite has been reported in our previous paper [29]. The GE-dispersed nanofluids at mass fractions of 0.03% and 0.06% were prepared by ultrasonically dispersing GE in $[HMIM]BF_4$ using a 100 W, 40 kHz ultrasonicator for 8 h, followed by the ultrasonic cracking using a 25 W Ultrusonic Cell Disrupter System (JYD 900, Shanghai Zhisun Equipment Co., Ltd., China), respectively.

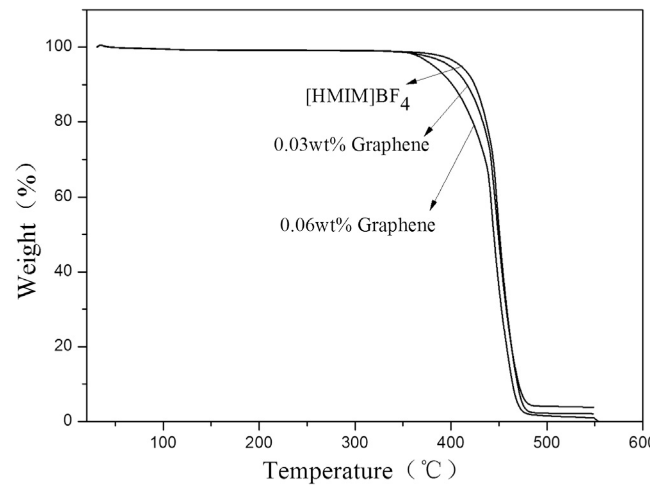

Fig. 1. Thermal conductivity of $[HMIM]BF_4$ and the GE-dispersed Ionanofluids as a function of temperature.

2.3. Characterization and measurements

The TC of the samples was measured at the temperature ranging from 25 to 200 °C using a thermal constants analyzer (Hot Disk TPS 2500S, Hot Disk AB, Sweden). In order to precisely control the temperature, a cyclic phenylmethyl silicone oil bath was applied. After every increase in temperature, the samples were equilibrated for at least 5 min before tested. The measurement was repeated for three times, and average values were calculated in this paper. The measurement accuracy of the TC was within ±3%.

The viscosity of the samples was measured by a viscometer (DV-I, Brookfield, USA) that with a specified accuracy of ±1.0% at a revolution rate of 100 RPM. Each sample was measured at the temperature ranging from 30 to 210 °C with the help of a thermal thermostatic magnetic stirrer equipped with phenylmethyl silicone oil.

The specific heat of the samples was evaluated with a differential scanning calorimeter (DSC, Q20, TA Instruments, USA) by the sapphire method. The temperature was kept at 25 °C for 5 min, and then ramped to 215 °C at the increasing rate of 10 °C min^{-1} followed by keeping for another 5 min. To validate the accuracy of the measuring method, the specific heat of distilled water was measured at different temperature. It is found that the measured values are very close to the standard data for the specific heat of distilled water at the same temperature. The measurement uncertainty only ranges from 0.2% to 0.9%.

The density of the samples was obtained as follows. Firstly, all samples were poured into measuring cylinders with the same volume, and then the cylinders were weighed in an electronic analytical balance. Secondly, the cylinders filled with samples were heated from 30 to 210 °C by a thermal thermostatic magnetic stirrer equipped with phenylmethyl silicone oil. At each temperature, the volume of the fluid was recorded. The density of each sample was calculated by the following formula: $\rho = m/V$, where m represents the weight of the samples (unit: g), and V represents the volume of the samples (unit: cm^3). The measurement accuracy of density is ±0.0001 g cm^{-3}.

The thermogravimetric analysis (TGA) was performed on an STA 449C thermal analyzer (NETZSCH, Germany). Measurement was conducted by heating the samples from room temperature to 550 °C at a heating rate of 10 °C min^{-1} under nitrogen flowing.