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Thermally Conductive of Nanofluid from Surfactant Doped Polyaniline Nanoparticle and Deep Eutectic Ionic Liquid

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Abstract. Nanofluid is a colloidal suspension of nano-size particles in a fluid. Spherical shape dodecylbenzenesulfonic acid doped polyaniline (DBSA-PANI) nanoparticles were synthesized via reverse micellar polymerization in isooctane with average size of 50 nm- 60 nm. The aim of study is to explore the possibility of using deep eutectic ionic liquid (DES) as a new base fluid in heat transfer application. DES was prepared by heating up choline chloride and urea with stirring. DES based nanofluids containing DBSA-PANI nanoparticles were prepared using two-step method. Thermal conductivity of nanofluids was measured using KD2 *Pro* Thermal Properties Analyzer. When incorporated with DBSA-PANI nanoparticles, DES with water was found to exhibit a bigger increase in thermal conductivity compared to that of the pure DES. The thermal conductivity of DES with water was increased by 4.67% when incorporated with 0.2 wt% of DBSA-PANI nanoparticles at 50°C. The enhancement in thermal conductivity of DES based nanofluids is possibly related to Brownian motion of nanoparticles as well as micro-convection of base fluids and also interaction between dopants and DES ions.

Keywords: conducting polymer, colloidal chemistry, ionic liquids, thermal conductivity
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INTRODUCTION

Nowadays, nanofluids become important in various applications, such as engineering and medical [9]. Nanoparticles were used as filler due to their high surface area compared to micrometer or millimeter sized solid particles [5,9]. Nanofluids have good stability and excellent thermal properties, so that problems of pressure drop and erosion in microchannels can be avoided [2].

Various ionic liquids are used as base fluids in nanofluids, such as pyridinium and imidazolium ionic liquids. The term of ionanofluid was defined as dispersion containing nanomaterials and ionic liquids [10]. Ionic liquids are advanced due to their high density, good heat capacity, good thermal and chemical stability and low vapor pressure [13]. The enhancement in thermal conductivity of several ionic liquids ([$C_n$mim][NTf_2] (where n =4, 6, and 8), [C_4mim][CF_3SO_3], [C_2mim][$EtSO_4$], [C_4mim][BF_4] and [C_4mim][PF_6]) was obtained with incorporation of multiwall carbon nanotube and single carbon nanotube [11]. Ionanofluids (1-butyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}imide ([C_4min][NTf_2]) and N-butyl-N-methylpyrrolidinium bis{(trifluromethyl) sulfonyl}imide ([C_4mpyrr][NTf_4]) containing aluminium oxide were reported. Thermal conductivity, specific heat capacity and heat transfer coefficient were increased by 6%, 23% and 20% respectively when 1wt% of Al_2O_3 nanoparticles were incorporated into ionic liquids [12]. Thermodynamic properties of graphene-dispersed nanofluids based on 1-hexyl-3-methylimidzolium tetrafluoroborate ([HMIM]BF_4) at different temperature were studied. Thermal conductivity of nanofluids was enhanced with increasing temperature while specific heat capacity, viscosity and density of nanofluids were decreased [6]. Due to these enhanced thermal properties, ionic liquids become good candidate as heat transfer fluids. However, the cost and toxicity of ionic liquids are high [20].

Deep eutectic ionic liquid (DES) is a new class of eutectic liquid that is formed by quaternary ammonium salt and hydrogen bond donor, such as (amines, acids, alcohols) [8]. They have the physico-chemical properties similar to conventional ionic liquids. They are mixtures of compounds that have lower melting point than their individual components. DESs are widely applied for dissolution, catalysis, organic synthesis, electrochemistry and electrolyte [19]. DESs are low cost raw materials, easy in the preparation without purification process, non-toxic and biodegradable [14, 4]. The most important is DESs have high mobility and high concentration of carrier ions and it

improves ionic conductivity [15]. Hence, it is expected to improve thermal conductivity. Due to these advantages, conventional ionic liquids can be replaced with DESs [1].

This study was carried out to explore the possibility of using DES as a new base fluid in nanofluids. Thermal conductivity of deep eutectic ionic liquids based nanofluids containing DBSA-PANI nanoparticles was investigated.

EXPERIMENTAL

Materials

The aniline monomer was purified before it was used for synthesis while other chemicals were directly used. All chemicals were purchased from Acros Oganic Company. Deionised water was used throughout the whole experiment.

Synthesis of Dodecylbenzenesulfonic Acid Doped Polyaniline (DBSA-PANI) Nanoparticles

The synthesis was carried out according to report by Han et al. [3], with slight modification, DBSA (0.04 moles) was dissolved in isooctane (50 mL) while APS (0.01 moles) was dissolved in deionised water (5.0 mL). The aqueous APS solution was added into DBSA solution to form a homogeneous solution (A) and stirred for 30 minutes. At the same time, aniline (0.02 moles) was added into isooctane (25 mL). Ethanol (1.0 mL) was later dropped into it and stirred for 30 minutes to obtain a homogeneous solution (B). The B solution was added into A solution. The mixture was stirred with 400 rpm for 24 hours. The precipitate was washed with deionised water and methanol for several times in order to remove unreacted aniline, free DBSA and impurities. The filtrate was dried in a vacuum oven at 60°C for 24 hours. The dried product was ground into ultrafine powder.

Preparation of Deep Eutectic Ionic Liquid (DES)

Choline chloride and urea were mixed and heated at 90°C to form a colourless eutectic mixture (pure DES). When the temperature of mixture dropped to room temperature, deionised water (15 wt%) was added into the mixture and stirred for 15 minutes (DES with water). The molar ratio of quaternary salt and hydrogen bond donor was fixed at 1:2.

Preparation of Nanofluids from Synthesized DBSA-PANI Nanoparticles and DES

DBSA-PANI nanoparticles were physically mixed with DES and water. The suspension was placed under ultrasonic bath for 2 hours to obtain a homogenous mixture. The mass fraction was varied from 0.2% to 1.0%. 0.2% of DBSA-PANI nanofluid was prepared with dispersing 0.02 g DBSA-PANI nanoparticles into 9.98 g DES with water. Same preparation method was repeated with pure DES.

Characterization of DBSA-PANI Nanoparticles

The morphology and size of DBSA-PANI were investigated by FESEM SUPRA 55VP (Zeiss Germany). The FTIR spectra of sample were prevailed on a Perkin Elmer Spectru, GX over a frequency range of 650 cm^{-1} – 4000 cm^{-1} at a scanning resolution of 4 cm^{-1}.

Thermal conductivity of nanofluids was measured using KD2 Pro Thermal Analyzer (Decagon Devices, Inc., USA). The KS-1 sensor needle is designed for measuring thermal conductivity of liquids. It is made up stainless steel having length of 60 mm and a diameter of 30 mm. It most close approximates the infinite line heat source and cause the least disturbance to the samples, so it gives the most accurate results. Before any measurement, the analyzer was calibrated with deionised water and glycerin. The temperature of water bath was adjusted to 30°C, 40°C and 50°C. The temperature of sample should be kept constant as the temperature of water bath for 15 minutes before measurements.
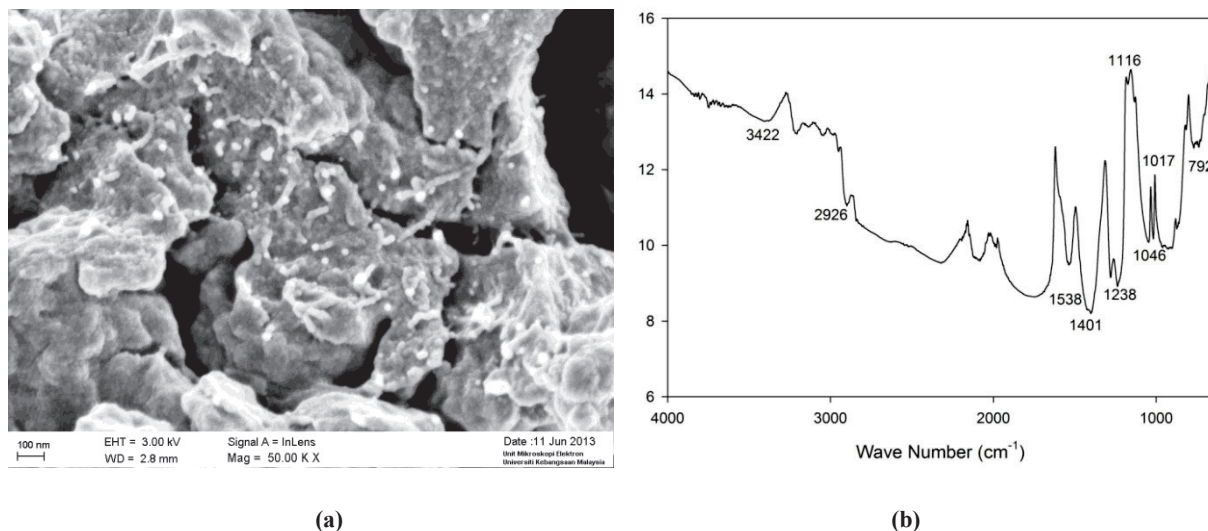
RESULTS AND DISCUSSION

(a)

(b)

FIGURE 1. FESEM micrograph (a) and FTIR spectrum of DBSA-PANI nanoparticles (b).

Spherical DBSA-PANI nanoparticles were obtained with average size of 50 nm to 60 nm (FIGURE 1 (a)). Clusters of DBSA-PANI nanoparticles were formed due to strong force of attraction between each nanoparticle. In the spectrum FTIR spectra of DBSA-PANI nanoparticles (FIGURE 1 (b)), bands near 1538 cm^{-1} and 1401 cm^{-1} were assigned to stretching of C=C of quinoid ring and C=C of the benzenoid ring. C-N stretching, N=Q=N mode stretching and C-H stretching were shown at 1238 cm^{-1}, 1116 cm^{-1} and 792 cm^{-1}. These bands were assigned to the PANI chains. At the same time, >CH of benzenoid ring stretching, S=O stretching, C-H(CH$_2$) stretching and O-H stretching were shown at 1017 cm^{-1}, 1046 cm^{-1}, 2926 cm^{-1} and 3422 cm^{-1}. These bands were assigned to DBSA molecules as dopants. It indicated that PANI was successfully doped with DBSA molecules.
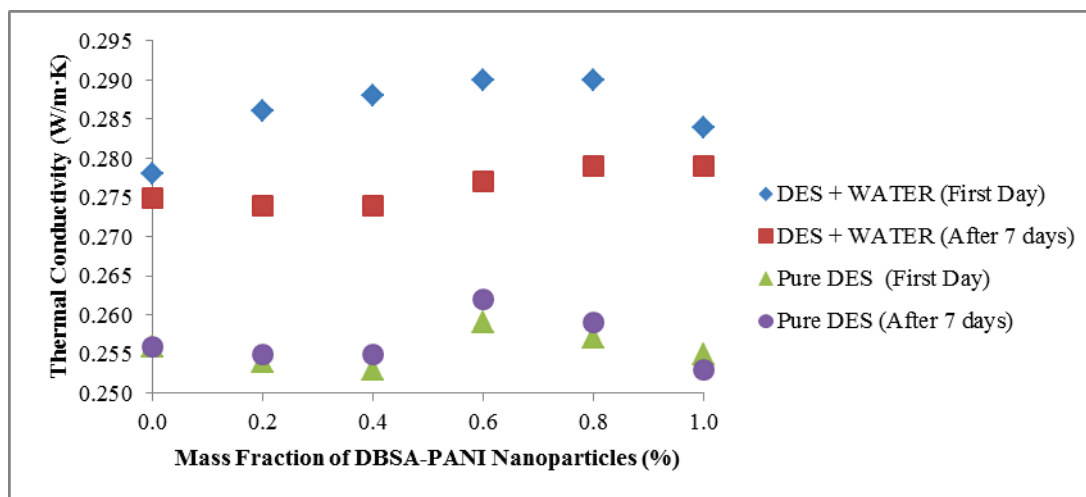

FIGURE 2. Thermal conductivity of DES based nanofluids with various mass fraction of DBSA-PANI nanoparticles.

Incorporation of DBSA-PANI nanoparticles enhanced the thermal conductivity of the DES (FIGURE 2). The enhancement in the thermal conductivity of DES with water was more pronounced than pure DES. 4.32% of enhancement in thermal conductivity of DES with water was achieved when adding 0.8% of mass fraction of DBSA-PANI nanoparticles. However, thermal conductivity of pure DES based nanofluids containing DBSA-PANI nanopartilces was almost constant. After one week, the thermal conductivity of DES with water based nanofluids

decreased because the agglomeration of nanoparticles became more significant. As a result, interfacial interaction between solid and fluid was reduced. The nanoparticles became larger and settled down in DES hence it affected the stability of nanofluids.
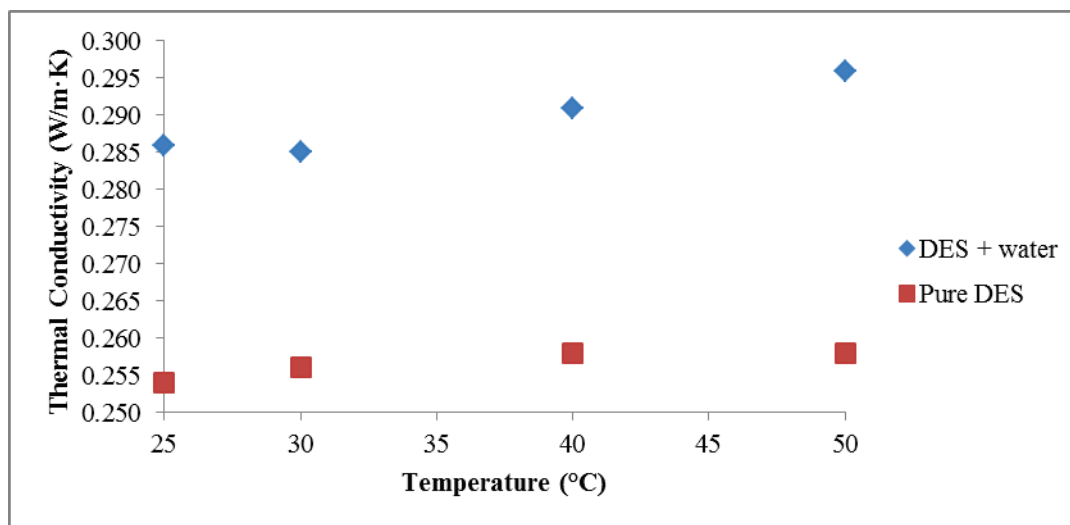

FIGURE 3. Thermal Conductivity of DES based nanofluids containing 0.2 wt% of DBSA-PANI nanoparticles as a function of temperature.

FIGURE 3 shows plots of thermal conductivity of DES based nanofluids containing 0.2 wt% of DBSA-PANI nanoparticles as a function of temperature. When the temperature was increased, the thermal conductivity of DES with water based nanofluids was enhanced, however, the thermal conductivity for pure DES based nanofluids showed much smaller increase. The mechanism of enhancement in thermal conductivity is expected to be related to Brownian motion of nanoparticles and micro-convection of base liquids [16-17]. The mechanism was pronounced at low concentration of nanoparticles. Nanoparticles gained and transferred more thermal energy through collision and convection. In this study, DBSA-PANI nanoparticles acted as surfactant and dopant [3]. DBSA modified the surface of nanoparticles and improved the stability of nanofluids [2,7] while water played as another hydrogen bond donor in this case [10,18]. Interaction of dopants and DES ions was also revealed to contribute to enhancement in thermal conductivity of DES based nanofluids.

CONCLUSION

Spherical PANI nanoparticles were successfully doped with DBSA using reverse micellar polymerization in isooctane with average size of 50-60 nm. These were prevailed with characterization of FESEM and FTIR. DES based nanofluids were produced using two-step method. Thermal conductivity of DES with water was enhanced with increasing mass fraction of DBSA-PANI nanoparticles and temperature. Enhancement in thermal conductivity DES with water nanofluids containing 0.2 wt% of DBSA-PANI nanoparticles was 6.47% at 50°C. Minimum enhancement in thermal conductivity of pure DES was observed as incorporation upon DBSA-PANI nanoparticles when temperature was increased. Mechanism of enhancement in thermal conductivity is thought to be related to Brownian motion of nanoparticles and micro-convection of base liquids. Interaction between dopants and DES ions might be contributed to this enhancement in thermal conductivity.

ACKNOWLEDGEMENTS

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