

THEORETICAL MODELLING OF THERMAL CONDUCTIVITY OF DEEP EUTECTIC SOLVENT BASED NANOFLUID

OSAMA M.¹, RASHMI W.^{1,*}, KAVEH S.¹, KHALID M.², GUPTA TCSM³

¹Energy Research Group, Department of Chemical Engineering, School of Engineering, Taylor's University Lakeside Campus, Malaysia

²Division of Manufacturing and Industrial Processes, Faculty of Engineering, University of Nottingham, Jalan Broga, 43500, Semenyih, Selangor, Malaysia

³Apar Industries, Research and Development, Chembur, Mumbai, India

*Corresponding Author: rashmigangasa.walvekar@taylors.edu.my

Abstract

In this research, the thermal conductivities of graphene oxide nano-particles (GO) dispersed in deep eutectic solvents (DESs) composed of ethylene glycol (EG) as a hydrogen bond donor (HBD) and methyl tri-phenyl phosphonium bromide (MTPB) as a salt, at weight fractions of 0.01%, 0.02% and 0.05%, were studied and quantitatively analysed. The molar ratios of DES (HBD:Salt) used in this study are 3:1 and 5:1. The thermal conductivity data of the nano-fluid samples were measured at temperatures of 25-70 °C and the results were compared with theoretical models. Rashmi and Kumar's models showed conflicting prediction performance. While, Rashmi's model can predict thermal conductivity with error as low as 0.1%, Kumar's model error varied from 3-55%. Thus, in this work, a simple empirical modification to Kumar's model is presented which improves the predictions accuracy compared to that of Rashmi's model.

Keywords: Nano-fluid, DES, Graphene oxide, Thermal conductivity.

1. Introduction

Nano-fluid is a stable suspension of nano-sized materials in a base liquid. Nano-scale materials may come in a variety of forms such as nano-rods, nano-composites, nano-fiber, nano-wire, nano-sheet, nano-particle, nano-tube, nano-bubble and nano-droplet [1]. Nano-fluids were first proposed by Choi and since then gained popularity in the field of research [2]. The development of the nano-fluids was the direct result of efforts to improve the thermal conductivities of heat transfer fluids. This is complementary to the development of energy-effective heat

Nomenclatures

a	Particle/liquid molecule radius, m
C	Constant
d	Particle diameter, m
k	Thermal conductivity coefficient, W/m.K
k_B	Boltzmann constant, J/K
l	Particle length, m
T	Temperature, °C

Greek Symbols

ϕ	Volume fraction
μ	Fluid dynamic viscosity, kg/m.s

Subscripts

be	Base fluid
eff	Effective property of nano-fluid
p	Nano-particle

transfer devices. Choi [3] proposed that new class of heat transfer liquids can be prepared by suspending metallic nano-particles in conventional heat carrier fluids.

The idea of improving thermal properties of a fluid by the dispersion of solid particles is antique. Due to their extremely large thermal conductivities, it was expected that the mixing and dispersion of metallic solid particles in fluids would enhance thermal conductivities of the host fluids. Indeed, Maxwell's model which was published more than 100 years shows that the effective thermal conductivity of a colloidal suspension containing spherical particles increases with the volume fraction of solid particles [3]. The initial studies of solid dispersion were confined to micron-sized particles. However, due to their relatively large size, they are prone to flow clogging problems. On the other hand, nano-particles are smaller and thus will not be prone to flow blocking issues as much. In addition, nano-sized particles have extremely large surface area to volume ratio which is known to increase thermal conductivities of fluids [3]. Though, as time elapses, nano-particles are prone to self-agglomeration due to their high surface energy. The agglomerates size can be as large as micron-sized particles. These large agglomerates are prone to sedimentation which lowers the enhancement of thermo-physical properties [1].

Earlier experiments on nano-fluids showed that the thermal conductivity enhancement goes beyond predictions by the classical model of Maxwell [4]. In some cases, up to 40% enhancement have been recorded at nano-particles volume fraction as low as below 1% [5]. Meanwhile, other experiments have shown moderate enhancement which is consistent with Maxwell's model, along with this even substantially larger enhancements have been recorded [5]. This inconsistency highlights the difficulty in producing standardized and consistent nano-fluid samples. By then, it was established that the thermal conductivity enhancement in nano-fluids is a function of other parameters such as host-fluid type, nano-particles characteristics, nano-particles size, nano-particles shape, spatial distribution, temperature and pH value [4].

Traditionally, the nano-fluid preparation has been researched on conventional heat carriers such as water and synthetic oil. Adding to their low thermal performance, the stability of nano-suspension in these base fluids is rather limited to the use of additives. New class of fluids has emerged known as ionic liquid which has thermo-physical properties far superior to conventional liquids. Wang et al. [6], prepared nano-fluid based on ionic liquid using graphene nano-particles. Their result showed considerable thermal conductivity enhancement and more homogeneity of dispersants when compared to multi-walled carbon nano-tubes. Unfortunately, many reports have pointed out the hazardous toxicity of ionic liquids along with their expensive synthesis [7]. This has led to the emergence of deep eutectic solvents (DES) which are far more environmentally friendly owing to their biodegradability and non-toxicity. Along with that, their synthesis is far cheaper and they do exhibit similar thermos-physical properties as ionic liquids [7].

Graphene is a single layer of graphite. It is composed of hexagonally oriented carbon atoms. The thermal conductivity of graphene is among the highest, in some papers the thermal conductivity of graphene is reported in the range of 2000–4000 W/m.K. The lower end is typically found in mixed isotope samples, meanwhile purified isotopes can approach the upper end [8]. There are even estimates as high as 5000 W/m.K for the thermal conductivity of graphene. For instance, Balandin et al. [9] reported that the thermal conductivity of single layer of graphene is ~5300 W/m.K which is higher than that of carbon nano-tubes. In nano-fluid literature, different combinations of graphene nano-particles were used. For instance, Baby and Ramaprabu [10], used hydrogen exfoliated graphene nano-fluids and their results showed considerable enhancement of thermal conductivity. Among these combinations, graphene oxide nano-particles (GONPs) are of a great significance. This is due to the presence of additional carbonyl and carboxyl groups located at the edge of the graphene, making it strongly hydrophilic [11]. Hydrophilic surface is desired in particles, because it improves dispersion in base fluids.

In the current work, GONPs were dispersed in DES base fluid composed of methyl tri-phenyl phosphonium bromide (MTPB) as a salt and ethylene glycol as hydrogen bond donor (HBD). The DES nano-fluid was prepared under two different molar ratio combinations of the aforementioned salt and HBD. The thermal conductivities of the prepared DES nano-fluid samples were measured and compared with thermal conductivities predictions obtained using two Brownian based models, namely Rashmi's model [12] and Kumar's model [13]. A necessary modification was made to the Kumar model to improve its predictions capability. The new model is referred to as Kumar's modified model.

2. Method

2.1. Materials

The ethylene glycol and MTBP chemicals were obtained from Merck Millipore at a high purity of > 99%. These chemicals were used to synthesize the DESs at different molar ratios. The graphene nano-particles were purchased from the Graphene Supermarket, United States with high purity of 98%. The graphene nano-powder has an average thickness of 60 nm and a particle size in the range of 3-7 microns.

2.2. Functionalization of graphene

The graphene nano-particles (GNPs) were functionalized to produce GONPs using the Simplified Hammer method. Eight tenths grams of graphene was added to a solution containing sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). The solution was prepared at a ratio of 4:1 of sulfuric acid and phosphoric acid respectively. The volumes added of sulfuric and phosphoric acids are 320 ml and 80 ml respectively. Then, the graphene powder was added to the mixture along with 18 g of potassium permanganate ($KMnO_4$). The mixture was allowed to be stirred for three days. After that, 300 ml of deionized water and 50 ml of hydrogen peroxide (H_2O_2) were added to the mixture upon which the solution turned to bright yellow colour from brown colour. Moreover, a ratio of 1:10 of hydrochloric acid (HCl) and deionized water solution was added to the mixture. Then, the suspension was water-washed using centrifuge (HettichZentrifugen, Universal 320 R) until the pH value of the filtrate was close to 7. Sodium Hydroxide (NaOH) solution was added to fasten the neutralization process. After the pH value was close to 7, the suspension was left for approximately two days to dry in an oven with a temperature-set of 60 °C.

2.3. DES based nano-fluid synthesis

In this research graphene oxide nano-particles were dispersed in one DES base fluid synthesized at two different combinations of the same hydrogen bond donor (HBD) and salt. The HBD used is ethylene glycol and the salt is MTPB. The DES base fluids were prepared by mixing the salt with the HBDs in the prescribed molar ratios as shown in Table 1 using a magnetic stirrer at 90 – 100 °C, and 900 – 1500 rpm until a homogenous and colourless liquid is observed. The DES nano-fluid was prepared at low weight fraction of GONPs. Wang et al. [6] stated that at weight fractions up to 0.09%, the graphene nano-particles Nano-fluid (NF) will not be stable and will coagulate in a couple of hours. In this study, 0.01%, 0.02% and 0.05% weight fractions were used. The graphene oxide nano-particles dispersed in the DES liquid were exposed to water-bath sonication for one hour, followed by probe sonication for 15 minutes carried at intervals of 5 minutes. Thus, sonication was carried for 5 minutes, stopped for 5 minutes and then the process is repeated until 15 minute sonication was achieved. Table 1 shows the labels used for each DES and NF samples.

Table 1. Graphene oxide nano-fluid (GNF) samples labelling code.

Molar Ratio (HBD:Salt)	DES Sample	NF Sample	GO wt%
3:1	DES 1	GNF 1	0.01
		GNF 2	0.02
		GNF 3	0.05
5:1	DES 2	GNF 4	0.01
		GNF 5	0.02
		GNF 6	0.05

2.4. Measurements and modelling of thermal conductivity

The used thermal conductivity data was measured for the DES based NF samples at temperatures 25-70 °C using KD 2 Pro. Table 2 shows Kumar and Rashmi' models which are used for evaluation in this research. The parameters of these models are volume fraction ϕ , thermal conductivity coefficient k of the nano-particle and the base fluid, l particle length, d particle diameter, a particle or liquid molecule radius, μ fluid viscosity and k_B the Boltzmann constant. The terms n , C and T_0 are constants. The subscripts *eff*, *bf*, *p* refer to the effective property of nano-fluid, base-fluid and nano-particles respectively. The density of the graphene oxide used in the calculations is 2.2 g/cm³, moreover a thermal conductivity value of 5000 W/m.K was assumed for the graphene oxide nano-particles.

Table 2. Thermal conductivity models.

Ref.	Model Name & Formulation
Rashmi et al. [12]	$k_{eff} = k_{bf} \left[1 + \frac{k_p \frac{2\phi(a_p + l_p)}{a_p l_p}}{k_{bf} \left(\frac{3(1-\phi)}{a_{bf}} \right)} \right] + \frac{C\phi(T - T_0)}{a_{bf}^2 l_{bf}^2 \mu_{bf}} \ln\left(\frac{l_p}{d_p}\right)$
Kumar et al. [13]	$k_{eff} = k_{bf} + c \frac{2 k_B T \phi a_{bf}}{\pi \mu d_p^2 (1 - \phi)}$

Rashmi's model [12] is derived from Patel's model [13] which was modified to suit application of nano-tube shaped particle (such as CNT) and the liquid molecule is assumed to be spherical in shape [12]. Rashmi's model [12] considers the effect of Brownian motion. Kumar's model [13] is composed of two sub-models, namely the stationary particle model and the moving particle model [14]. The ability for Rashmi's model [12] and Kumar's model [13] to predict the behaviour of DES based nano-fluid was examined by attempting to fit them with the experimental data and the quality of the resulting plot indicated how well each model predicts the behaviour of the current DES based nano-fluid. This was done by the grouping the unknown sub-variables and constants into one main or clustered variable. Accordingly, Rashmi's model and Kumar's model were simplified to the form shown in Eqs. (1) and (2), respectively.

$$k_{eff} = k_{bf} + \frac{k_p \phi C_0}{(1-\phi)} + C_1 \phi (T - T_0) \quad (1)$$

$$k_{eff} = k_{bf} + \frac{\phi}{(1-\phi)} T C_2 \quad (2)$$

The constants C_0 and C_1 in Eq. (1) and the constant C_2 in Eq. (2) are illustrated in Eqs. (3), (4) and (5) respectively.

$$C_0 = \frac{\frac{2(a_p + l_p)}{a_p l_p}}{\left(\frac{3}{a_{bf}} \right)} \quad (3)$$

$$C_1 = \frac{c}{a_{bf}^2 l_{bf}^2 \mu_{bf}} \ln\left(\frac{l_p}{a_p}\right) \quad (4)$$

$$C_2 = c \frac{2 k_B}{\pi \mu a_p^2} a_{bf} \quad (5)$$

In order to examine how well the collected data, fit with Rashmi's model and Kumar's model, the equations were rearranged to resemble a linear equation in the form $y = m X + c$. The linearized forms were fitted with the thermal conductivity data at a fixed temperature. The linear forms are shown in Eqs. (6) and (7) for Rashmi's model and Kumar's model respectively.

$$\frac{k_{eff} - k_{bf}}{\phi (T - T_0)} = \frac{k_p C_0}{(T - T_0)(1 - \phi)} + C_1 \quad (6)$$

$$\ln(k_{eff} - k_{bf}) = \ln\left(\frac{\phi}{(1 - \phi)}\right) + \ln(T C_2) \quad (7)$$

As it can be seen from Eq. (6), the Y (dependent variable) is $(k_{eff} - k_{bf}) / (\phi (T - T_0))$ and the X (independent variable) is $1/(1 - \phi)$. From Eq. (7), the Y variable is $\ln(k_{eff} - k_{bf})$ and the X variable is $\ln(\phi/(1 - \phi))$. It can be noticed that while the linearized form of Rashmi's model [12] offers flexibility for changing slopes, the linearized form of Kumar's model has fixed slope $m = 1$. To account for this, an empirical modification for Kumar's model was made by including a power variable which controls the volume fraction term in Kumar's model [13]. The new model is named Kumar's modified model and it is illustrated in Eq. (8).

$$k_{eff} = k_{bf} + \left(\frac{\phi}{(1 - \phi)}\right)^n T C_0 \quad (8)$$

3. Results and Discussion

3.1. Prediction quality

The quality of the prediction obtained by different models was assessed using the percentage deviation from the actual behaviour. The results show that the quality of predicting the thermal performance of the DES based nano-fluid under research for each model depends on the surrounding temperature and the molar ratio of HBD to salt. Table 3 shows the average percentage of deviation of each model with respect to DES 1, DES 2 and the overall deviation.

Table 3. Percentage of deviation from actual behavior.

Model	Rashmi's model	Kumar's model	Kumar's modified model
DES 1 Deviation%	9.2	26.7	3.6
DES 2 Deviation%	5.8	20.4	6.6
Overall Deviation%	7.5	23.55	5.1

It can be seen from Table 3 that Rashmi's model [12] shows prediction capability that is slightly lower than Kumar's modified model and significantly higher than Kumar's model [13]. Moreover, Rashmi's model [12] predicts thermal performance for DES 2 more often better than Kumar's modified model. The Kumar's modified model has the best predictions capability, while Kumar's model has the lowest. It can be noted as well the high deviation of Kumar's model when compared to the percentage deviation of Kumar's modified model and Rashmi's model. It can be concluded that the inclusion of the power n variable improves the prediction capability of Kumar's model [13]. Figures 1-6 show the actual thermal conductivity behaviour of DES 1 and DES 2, and the corresponding predictions obtained by Rashmi's model, Kumar's model and Kumar's modified model for each temperature.

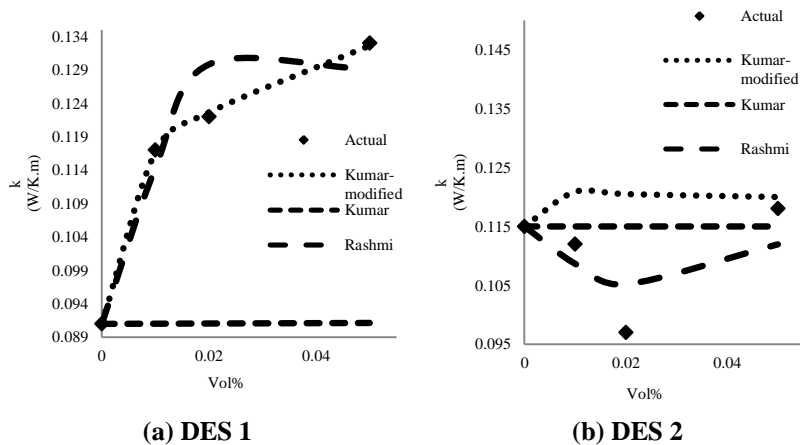


Fig. 1. Thermal conductivity predictions at $t = 25\text{ }^{\circ}\text{C}$.

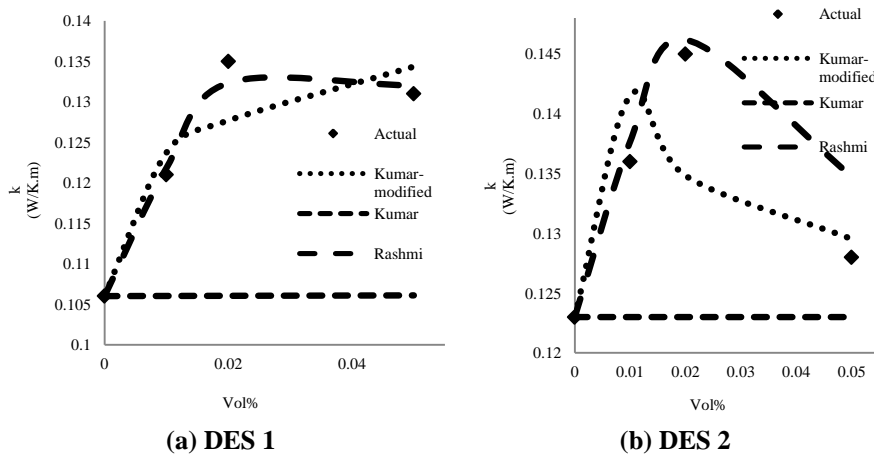


Fig. 2. Thermal conductivity predictions at $t = 30\text{ }^{\circ}\text{C}$.

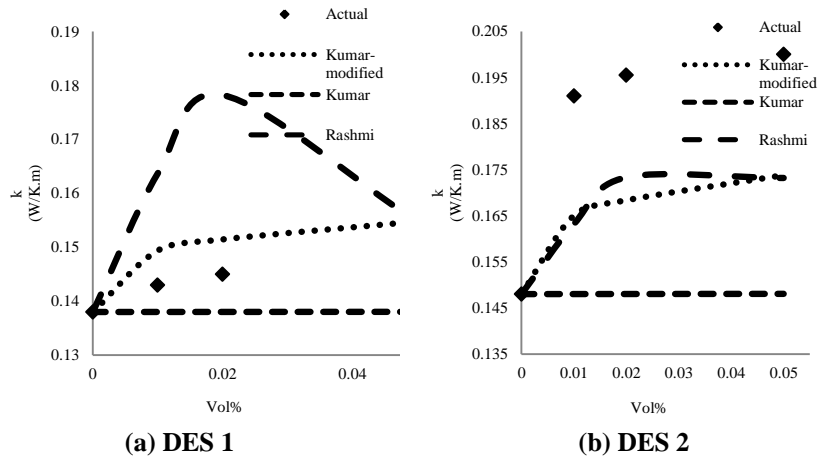


Fig. 3. Thermal conductivity predictions at $t = 40^\circ\text{C}$.

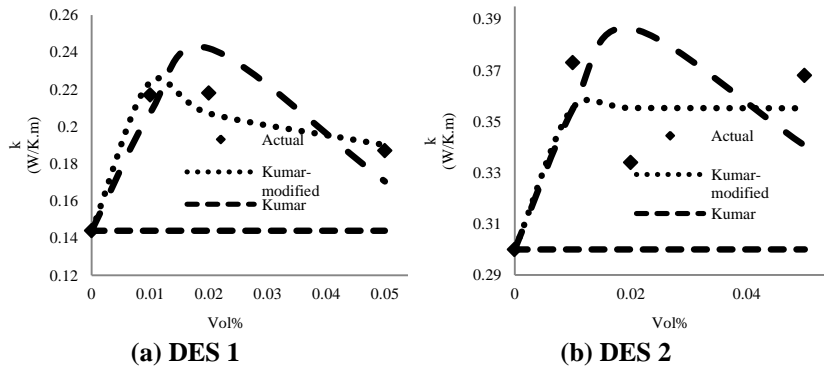


Fig. 4. Thermal conductivity predictions at $t = 50^\circ\text{C}$.

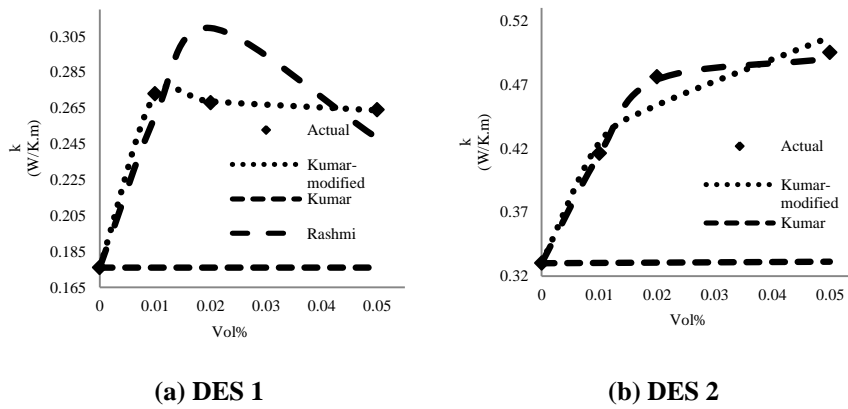


Fig. 5. Thermal conductivity predictions at $t = 60^\circ\text{C}$.

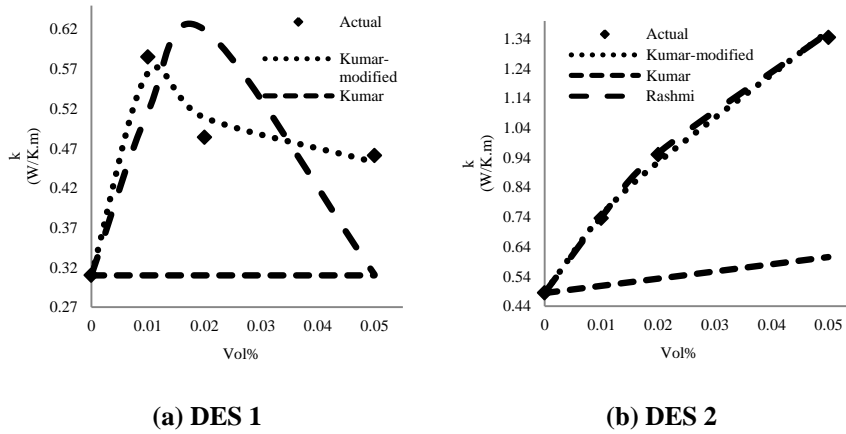


Fig. 6. Thermal conductivity predictions at $t = 70\text{ }^{\circ}\text{C}$.

As it can be seen from Figs. 1-6, at some temperatures the behavior of the DES 1 or DES 2 is consistent with the widely accepted and reported results that as the volume fraction of the nano-particles increases, higher enhancements are observed. At other temperatures, the behavior is rather messy and does not seem to follow specific pattern. Kumar’s modified model relatively predicts the behavior of DES 1 better than any other models as it can be seen from the left side graph in each of Figs. 1-6. The prediction capability of the behavior of DES 2 is generally lower than that of DES 1. The Kumar’s modified model and Rashmi’s model approximately predicts the behavior of DES 2 at the same accuracy as it can be seen from the right-side graph in each of Figs. 1-6.

3.2. Behaviour of n power variable

The behavior of the n power variable in Kumar’s modified model was found to change with temperature and composition. This trend can be observed in Fig. 7.

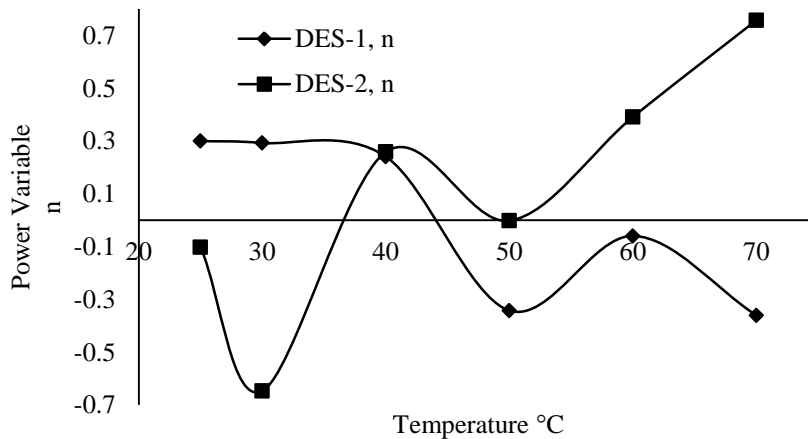


Fig. 7. Behavior of n power variable.

It can be seen from Fig. 7, that each DES has distinct curve. This suggests that the n power variable is a function of the molar ratio of HBD and the salt that constitutes the current DES. Moreover, the n variable is also a function of temperature. However, the relationship of n for each DES with respect to the temperature is very complex and somehow periodic. This is evident by the sign change of the slope for each DES curve at different temperatures.

4. Conclusions

In this research, the thermal conductivity of DES based nano-fluids was measured and compared with predictions obtained from theoretical models. The theoretical models that were used are Rashmi's model and Kumar's model. Kumar's model showed poor capability of predicting the current DES based nano-fluid. Fortunately, Kumar's model prediction capability can be improved by the inclusion of n power variable which controls the volume fraction term in Kumar's model. Kumar's modified model was found to have prediction capability that is approximately five times better than that of Kumar's model. Rashmi's model showed equally small deviation which is overall slightly lower than Kumar's modified model in terms of prediction capability. Moreover, it was found that Rashmi's model prediction capability is three times lower for DES 1 and one time better for DES 2 than that of Kumar's modified model. The n power variable was found to change with molar ratio of HBD to salt and the surrounding temperature.

Acknowledgement

The authors would like to acknowledge the Ministry of Higher Education (MOHE) for the financial funding of this research through Fundamental Research Grant Scheme (FRGS- FRGS/2/2013/TK06/TAYLOR/03/1).

References

1. Kostic, M.M. (2006). Critical issues and application potentials in nanofluids research. *ASME 2006 Multifunctional Nanocomposites International Conference*. Honolulu, Hawaii, USA, 1-49.
2. Taylor, R.; Coulombie, S.; Otanicar, T.; Phelan, P.; Gunawan, A.; Lv, W.; Rosengarten, G.; Prasher, R.; and Tyagi, H. (2012). Critical review of the novel applications and uses of nanofluids. *ASME 2012 Third International Conference on Micro/Nanoscale Heat and Mass Transfer*. Atlanta, Georgia, USA, 219-234.
3. Choi, S.U.S.; and Eastman, J.A. (1995). Enhancing thermal conductivity of fluids with nanoparticles. *International mechanical engineering congress and exhibition*. San Francisco, USA, 99-105.
4. Kleinstreuer, C.; and Feng, Y. (2011). Experimental and theoretical studies of nanofluid thermal conductivity enhancement: a review. *Nanoscale Research Letters*, 229(6), 1-13.
5. Eapen, J.; Rusconi, R.; Piazza, R.; and Yip, S. (2010). The Classical nature of thermal conduction in nanofluids. *Journal of Heat Transfer*, 132(10), 102402-102402-14.

6. Wang, F.; Han, L.; Zhang, Z.; Fang, X.; Shi, J.; and Ma, W. (2012). Surfactant-free ionic liquid-based nanofluids with remarkable thermal conductivity enhancement at very low loading of graphene. *Nanoscale Research Letters*, 314(7), 1-7.
7. Zhang, Q.; Vigier, K.D.O.; Royer, S.; and Jerome, F. (2012). Deep eutectic solvents: syntheses, properties and applications. *Chemical Society Reviews*, 41(21), 7108-7146.
8. Pop, E.; Varshney, V.; and Roy, A.K. (2012). Thermal properties of graphene: Fundamentals and applications. *MRS Bulletin*, 37(12), 1273-1281.
9. Balandin, A.A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; and Lau, C.N. (2008). Superior thermal conductivity of single-layer graphene. *Nano Letters*, 8(3), 902-907.
10. Baby, T.; and Ramaprabhu, S. (2011). Enhanced convective heat transfer using graphene dispersed nanofluids. *Nanoscale Research Letters*, 289(6), 1-9.
11. Kuila, T.; Bose, S.; Mishra, A. K.; Khanra, P.; Kim, N.H.; and Lee, J.H. (2012). Chemical functionalization of graphene and its applications. *Progress in Materials Science*, 57(7), 1061-1105.
12. Rashmi, W.; Ismail, A.F.; and Khalid, M. (2012). Thermal conductivity of carbon nanotube nanofluid - Experimental and theoretical study. *Heat Transfer-Asian Research*, 41(2), 145-163.
13. Kumar, D.H.; Patel, H.E.; Kumar, V.R.R.; Sundararajan, T.; Pradeep, T.; and Das, S. K. (2004). Model for heat conduction in nanofluids. *Physical Review Letters*, 93(14), 144301.
14. Lee, J.H.; Lee, S.H.; Choi, C.J.; Jang, S.P.; and Choi, U.S. (2010). A review of thermal conductivity data, mechanisms and models for nanofluids. *International Journal of Micro-Nano Scale Transport*, 4(1), 269-322.