VISCOSITY AND DENSITY OF CUO NANOLUBRICANT

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ABSTRACT

This paper presents liquid kinematic viscosity and density measurements of a synthetic polyolester based copper (II) oxide (CuO) nanoparticle dispersion (nanolubricant) at atmospheric pressure for a temperature range from approximately 288 K to 318 K. The polyolester was a commercially available chiller lubricant. The CuO particles were approximately 30 nm-diameter, spherical, and well dispersed in the lubricant. Viscosity and density measurements were made for the pure base lubricant along with three nanolubricants with differing nanoparticle mass fractions (2.9 %, 5.6 % and 39.2 %).   The viscosity and the density were shown to increase with respect to increasing nanoparticle mass fraction. Correlations of the viscosity and the density are presented as a function of temperature and nanoparticle concentration. The measurements are important for the design of nanolubricants for heat transfer and flow applications.

1. INTRODUCTION

The U.S. National Nanotechnology Initiative (NNI) has supported an explosion of research in recent years including the investigation of the heat transfer properties of liquids with dispersed nano-size particles called nanofluids. Prior to the initiative, nanofluids research was mainly confined to thermal conductivity investigations. Eastman et al. (2001) found that the thermal conductivity of some nanofluids, with nanoparticles at a volume fraction of less than 0.4 % resulted in the nanofluid having an effective thermal conductivity that was more than 40 % greater than that of the pure base fluid. For this reason, lubricant based nanofluids, i.e., nanolubricants, are believed to have a great potential for the enhancement of heat transfer.

Recent studies by Kedzierski (2008) and Bi et al. (2007) have recommended the use of nanolubricants as a means for improving efficiencies of chiller and refrigerators, respectively. Viscosity measurements of potential nanolubricants for these applications will benefit both fundamental research and design considerations. For example, Kedzierski (2001) has shown that lubricant viscosity significantly influences the performance of boiling refrigerant/lubricant mixtures. The efficiency of the boiling process in a chiller is a key determinant in the overall efficiency of a chiller. In addition, compressors in refrigerators and chillers have specific requirements for lubricant viscosity. Redesign of either the compressor or the nanolubricant requires nanolubricant viscosity and density measurements to ensure proper lubrication.

2. TEST LIQUIDS

A commercial polyolester lubricant (RL68H)[1], commonly used with R134a chillers, with a nominal liquid kinematic viscosity of 72.3 mm$^2 \cdot$s^{-1} at 313.15 K was the base lubricant that was mixed with nominally 30 nm diameter copper (II) oxide (CuO) nanoparticles. Copper (II) oxide

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[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

(79.55 g/mol) has many commercial applications including use as an optical glass-polishing agent. A manufacturer used a proprietary surfactant at a mass between 5 % and 15 % of the mass of the CuO as a dispersant for the RL68H/CuO mixture (nanolubricant). The manufacturer made the mixture such that nominally 40 % of the mass was CuO particles. The mixture was diluted in-house to roughly a 3 % and a 5.8 % mass fraction of CuO[2] by adding neat RL68H and ultrasonically mixing the solution for approximately 24 h. The particle size and dispersion were verified by a light scattering technique several weeks after mixing. The particles were approximately 35 nm and well dispersed with little particle agglomeration (Sung, 2006).

3. MEASUREMENTS

3.1 Stabinger Viscometer
A Stabinger Viscometer was use to measure the dynamic viscosity and the density of the liquid nanolubricant at various temperatures between approximately 288 K and 318 K. During the measurements, the atmospheric pressure varied between 0.12 MPa and 0.09 MPa at an approximate altitude of 137 m above sea level at Gaithersburg, Maryland, USA. The viscometer uses a vibrating U-tube to determine the density. The kinematic viscosity report here is obtained by dividing the dynamic viscosity by the density.

The operation principle of the Stabinger Viscometer relies on rotating concentric cylinders. The liquid sample of a Stabinger Viscometer is contained in the annulus of a concentric cylinder where the inner cylinder is hollow and of less mass than the sample. This allows the inner cylinder to float freely and centered by centrifugal forces in the sample when the outer cylinder is spun by a rotating magnetic field. Viscous shear forces on the liquid transfer the rotation to the inner cylinder. Measurements on the inner cylinder are used to calculate the difference in speed and torque between the outer and inner cylinder, and thus, the dynamic viscosity. Wasp et al. (1977) have recommended concentric cylinder viscometers for use with solid-liquid suspensions. All calculations are internal to the instrument and the results are displayed on a LCD screen and printed on rolled paper.

3.2 Uncertainties
The viscometer-manufacturer quoted uncertainty for the 95 % confidence level for the kinematic viscosity and the density was ± 0.35 % and ± 0.5 kg·m^{-3}, respectively. The viscometer was used to measure the density and viscosity of a calibration fluid with a nominal density and viscosity at 293.15 K of 1320 mm^2·s^{-1} and 845.4 kg·m^{-3}, respectively. Residuals between the measurements and the calibration standard over the same temperature range of this study were within the quoted specifications of the manufacturer.

Using the comparison with the standard and the residuals of the regressions for each individual fluid, the uncertainties for the viscosity and density measurements for each fluid were calculated and are presented in Table 1. In general, the uncertainties increase with increasing nanoparticle mass fraction, which is likely due, in part, to variations in the sample composition between repeat test runs. For the neat lubricant (without nanoparticles) the uncertainty of the density and the viscosity is a respectable ± 0.01 % and ± 2 %, respectively. Adding CuO nanoparticles results in larger increases in the viscosity uncertainty than in the uncertainty of the density. As shown in Table 1, the uncertainty for the density and viscosity measurements, for all of the nanolubricants, was less than ± 0.5 %, and ± 30 %, respectively. The larger uncertainty in the viscosity was due to the greater sensitivity of the viscosity to between-run variations in mass fraction. The uncertainty of the CuO mass fractions and uncertainties of this study were: 40 % ± 0.5 %, 5.8 % ± 0.1 %, and 3 % ± 0.06 %. The mass fraction uncertainties are based on the uncertainty

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[2] The influence of the 3 % and the 5.8 % mass nanolubricants on refrigerant boiling was previously investigated by Kedzierski (2008).

for the 40 % CuO mass fraction that was supplied by the manufacturer of the nanolubricant. All uncertainties given in this manuscript are for the 95 % confidence level unless otherwise stated.

Table 1. Estimated uncertainty of viscosity and density measurements for 95 % confidence level

Property	RL68H	$x_m = 2.9$ %	$x_m = 5.6$ %	$x_m = 39.2$ %
Viscosity $(mm^2 \cdot s^{-1})$	± 2 (± 2 %)	± 25 (± 20 %)	± 36 (± 30 %)	± 69 (± 13 %)
Density $(kg \cdot m^{-3})$	± 0.1 (± 0.01 %)	± 0.2 (± 0.02 %)	± 0.4 (± 0.03 %)	± 7 (± 0.5 %)

4. RESULTS

4.1 Density
Figure 1 shows the measured density (ρ_m) of the nanolubricant mixtures versus temperature (T) at atmospheric pressure. The solid lines shown in Fig. 1 are linear best-fit regressions or estimated means of the data. Fifteen of the 880 measurements were removed before fitting because they were identified as "outliers" based on having both high influence and high-leverage (Belsley, et al., 1980). Table 2 gives the constants for the linear regression of the measured specific volume (ρ_m^{-1}) versus the measured temperature for the fluids tested here. The dashed lines to either side of the mean represent the lower and upper 95 % simultaneous (multiple-use) confidence intervals for the mean. From the confidence intervals, the expanded uncertainty of the estimated mean density for the 95 % confidence level was shown to increase with respect to the mass fraction of the CuO nanoparticles being ± 0.03 kg·m⁻³, ± 0.05 kg·m⁻³, ± 0.10 kg·m⁻³, and ± 1.7 kg·m⁻³ for the 0 %, 3 %, 5.8 %, and the 40 % mass fraction nanolubricants, respectively.
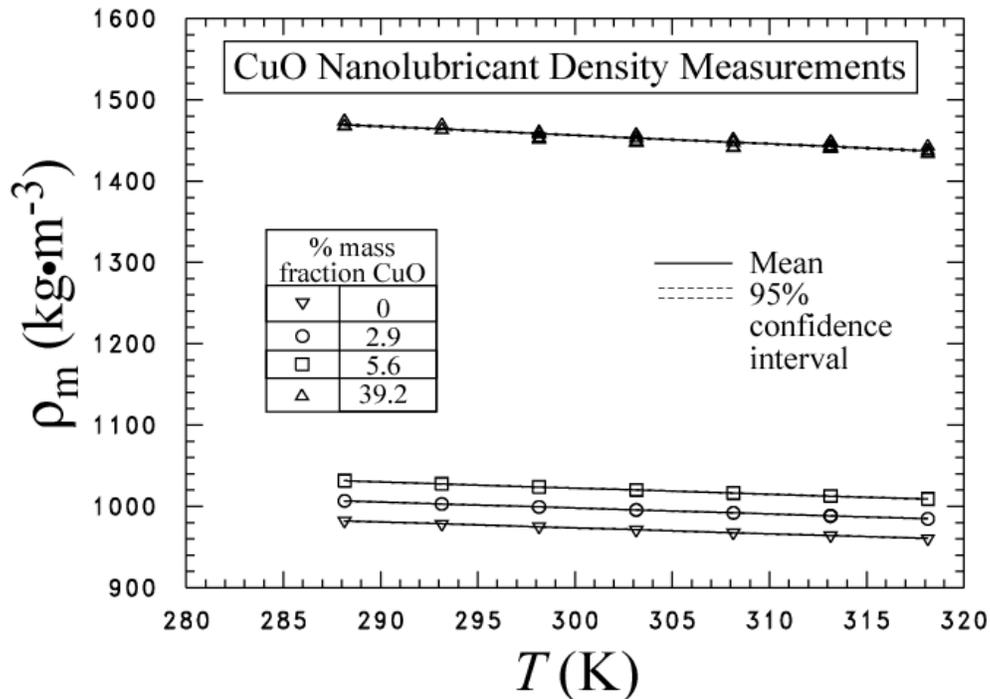

Figure 1 Measured liquid density of CuO nanolubricant for various mass fractions at atmospheric pressure

Table 2. Linear fit of density with respect to temperature: $\rho_p^{-1}[m^3 \cdot kg^{-1}] = B_0 + B_1 T[K]$

Fitting Constant	RL68H	$x_m = 2.9\%$	$x_m = 5.6\%$	$x_m = 39.2\%$
B_0	0.7979×10^{-03}	0.7794×10^{-03}	0.7611×10^{-03}	0.5368×10^{-03}
B_1	0.7647×10^{-06}	0.7425×10^{-06}	0.7232×10^{-06}	0.4992×10^{-06}

Figure 2 shows deviation between the measured density and the linear fits of the density (ρ_p) as given in Table 2 for all of the fluids. As shown in the plot, the residuals are all within $\pm 0.6\%$ for all of the fluids. Although it is not easily seen in Fig. 3 because of the scale, the residuals increase with nanoparticle mass fraction being $\pm 0.02\%$, $\pm 0.03\%$, and $\pm 0.04\%$ for the 0%, 3%, and 5.8% mass fractions, respectively. As explained above, the variation is likely due to small variations in the mass fraction that occurred between measurement runs with larger variations occurring at larger mass fraction.

Comparison of the nanolubricant density measurements to the recommended mixture equation for suspensions (Wasp et al., 1977):

$$\frac{1}{\rho_m} = \frac{x_m}{\rho_s} + \frac{1-x_m}{\rho_L} \tag{1}$$

results in an overpredition of the mixture density by approximately 0.2% and 1.5% for mass fractions less than and greater than 40%, respectively, when a CuO density[3] of 6310 kg·m^{-3} was used for the density of the solid nanoparticles (ρ_s) along with the correlated density values for the pure lubricant (ρ_L).
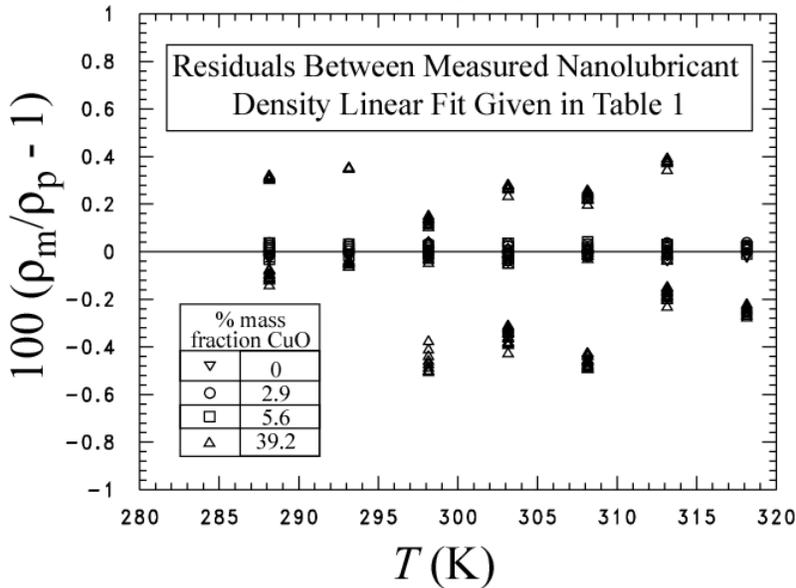

Figure 2 Residuals between measured nanolubricant density and linear fit of specific volume for all test fluids

In addition, Eq. (1) was also used to solve for the density of the CuO nanoparticles for the entire temperature range (288 K to 319 K), which resulted in an average density of 5760 kg·m^{-3} ± 12 kg·m^{-3} with random residuals with respect to temperature. The difference in this calculated density and the referenced value of 6310 kg·m^{-3} brings into question whether it is caused by a nanoscale phenomenon or a bias error in the original

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[3] http://www.nationmaster.com/encyclopedia/Copper%28II%29-oxide

CuO mass fraction as quoted by the manufacturer. Although, Grassian (2008) and Jamison et al. (2008) have shown that fundamental properties including density can be size dependent on the nanoscale, the author assumes that a bais error in the 40 % CuO mass fraction is responsible for the density discrepancy. Following this belief, Eq. (1) was used to correct the CuO mass fractions by setting the density of the solid particles to the referenced value of 6310 kg·m^{-3}. The back-substitution method gave corrected CuO mass fractions of 39.2 % $\pm$ 0.1 %, 5.6 % $\pm$ 0.02 %, 2.9 % $\pm$ 0.02 %.

4.2 Viscosity Measurements

Figure 3 shows the measured kinematic viscosity (v) of the nanolubricant mixtures versus temperature (T) at atmospheric pressure. The solid lines shown in Fig. 3 are three-parameter best-fit regressions or estimated means of the data to the following form for the normalized viscosity (v/v_0), which has been successfully used for 1944 compounds in the DIPPR Project17 (Rowley et al., 2007) and also by the NIST ThermoData Engine18 (Frenkel et al., 2007) and Outcalt et al. (2009):

$$\frac{v}{v_0} = \exp\left(A_0 + \frac{A_1}{T_r} + A_2 \ln(T_r) + A_3 T_r^{A_4} \right) \qquad (2)$$

where v_0 is the unity-viscosity ($v_0 = 1$ mm^2·s^{-1}), and T_r is the nanolubricant temperature normalized by 273.15 K. The term with the A_3 leading constant was found not to be statistically significant for the present data set. In addition, fifteen of the 880 measurements were removed before fitting because they were identified as "outliers" based on having both high influence and high-leverage (Belsley, et al., 1980). Table 3 gives the constants for the regression of the normalized kinematic viscosity versus the normalized temperature to Eq. (2) for the fluids tested
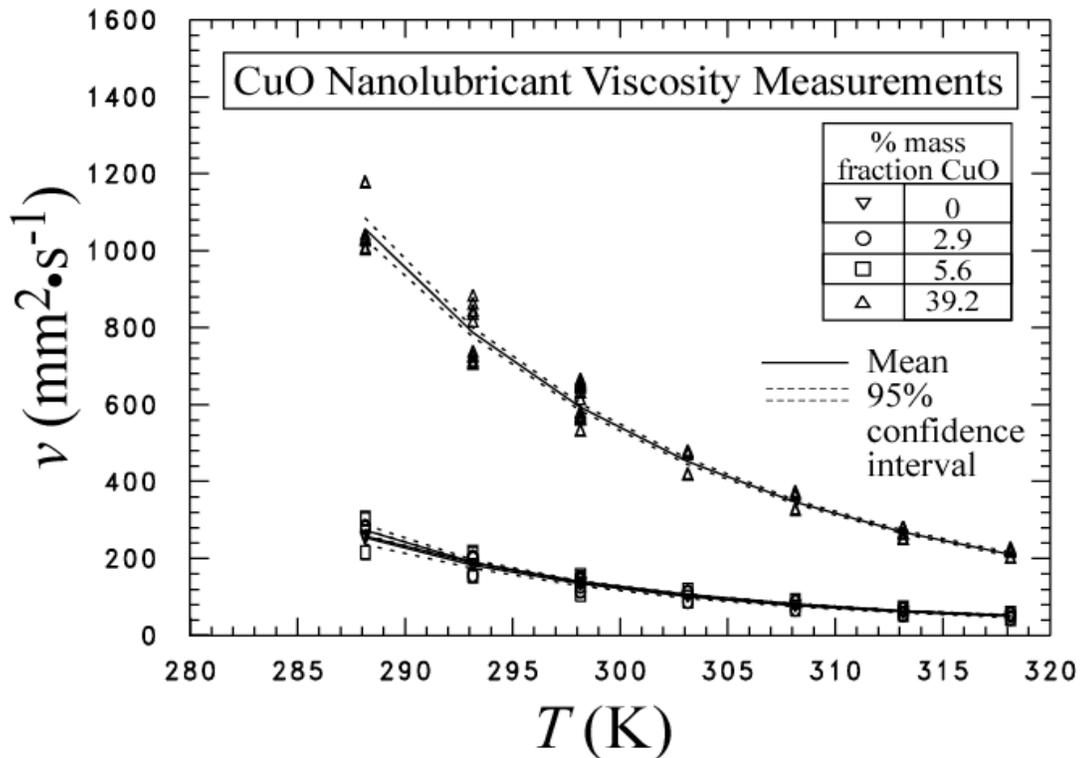

Figure 3 Measured liquid viscosity of CuO nanolubricant for various mass fractions at atmospheric pressure

here. The dashed lines to either side of the mean represent the lower and upper 95 % simultaneous (multiple-use) confidence intervals for the mean. From the confidence intervals, the expanded uncertainty of the estimated mean viscosity for the 95 % confidence level was shown to increase with respect to the mass fraction of the CuO nanoparticles being ± 0.5 mm^2·s^{-1}, ± 3.9 mm^2·s^{-1}, ± 6.7 mm^2·s^{-1}, and ± 10.2 mm^2·s^{-1} for the 0 %, 2.9 %, 5.6 %, and the 39.2 % mass fraction nanolubricants, respectively. The residuals for the fits given in Table 3 are within ± 15 % for all of the fluids. Although the relative percent residuals did not increase with respect to mass fraction, the absolute residuals did.

Table 3. Viscosity fit with respect to temperature: $\dfrac{v}{v_o} = \exp\left(A_0 + \dfrac{A_1}{T_r} + A_2 \ln T_r \right)$

Fitting Constant	RL68H	$x_m = 2.9$ %	$x_m = 5.6$ %	$x_m = 39.2$ %
A_0	-52.1976	-103.767	-11.7911	-10.1572
A_1	58.8482	110.709	18.2429	18.0583
A_2	36.8224	82.9465	0	0

5. DATA CORRELATION WITH RESPECT TO MASS FRACTION

The following section presents the correlation of the density with respect to CuO mass fraction (x_m). The viscosity was correlated with respect to the density.

5.1 Density
The resulting correlation of the liquid density of the base lubricant and the CuO nanolubricants to the CuO mass fraction at atmospheric pressure was:

$$\frac{1}{\rho}[\text{kg}^{-1}\text{·m}^3] = \left(7.627\times10^7 - 6.729\times10^7 x_m\right)T\,[\text{K}] + 7.984\times10^4 - 6.672\times10^4 x_m \tag{3}$$

where the density (ρ) has units of kg·m^{-3} while the input temperature (T) has units of kelvin. Equation (3) faithfully reproduced the individual fits giving the same residuals with respect to the measurements as shown in Fig. 3. More specifically, the residuals between the measure kinematic viscosity and the single correlation with respect to CuO mass fraction were ± 0.02 %, ± 0.03 %, ± 0.04 %, and ± 0.6 % for the 0 %, 2.9 %, 5.6 %, and 39.2 % mass fractions, respectively. Consistent with Eq. (1), Eq. (3) shows that the liquid density of the nanolubricant increases linearly with increasing CuO mass fraction.

5.2 Viscosity
The necessity of a fluid-specific correlation for the nanolubricants' viscosity was verified by comparing the measurements to the Stokes-Einstein equation (Einstein, 1956) for a dilute ($\phi < 0.6$) nanofluid with spherical nanoparticles:

$$\frac{v\rho}{v_L\rho_L} = 1 + (5/2)\phi \tag{4}$$

where ϕ is the volume fraction of the CuO nanoparticles. The viscosity measurements for the 0.45 % and the 0.9 % volume fractions (0.029 and 0.056 mass fractions, respectively) were centered about Eq. (4) and within ± 9 %. However, the 9 % volume fraction (39.2 % mass fraction) viscosity measurements were approximately six times the value given by Eq. (4).

Because of the poor prediction for the larger nanoparticle concentration, a fluid specific correlation is required for the nanolubricant viscosity.[4]

The resulting correlation of the liquid kinematic viscosity of the base lubricant and the CuO nanolubricants to the liquid density at atmospheric pressure was:

$$\nu[\text{mm}^2 \bullet \text{s}^{-1}] = 2.02 \times 10^{-5} \left(\frac{\rho}{1000[\text{kg} \bullet \text{m}^3]} \right)^{3.8} \exp\left(\frac{17.2}{T_r} \right) \tag{5}$$

where the kinematic viscosity has units of $\text{mm}^2 \cdot \text{s}^{-1}$ while the density (ρ) has units of $\text{kg} \cdot \text{m}^{-3}$. The density should be calculated from Eq. (3) and used as input for Eq. (5). Figure 4 shows that the single fit with respect to liquid density, i.e., Eq. (5), results in a slight increase in overpredicted residuals resulting in an approximate range of $+15\%$ and -25%. Equation (5) shows that the kinematic viscosity increases with respect to increasing density, i.e., increasing nanoparticle mass fraction.
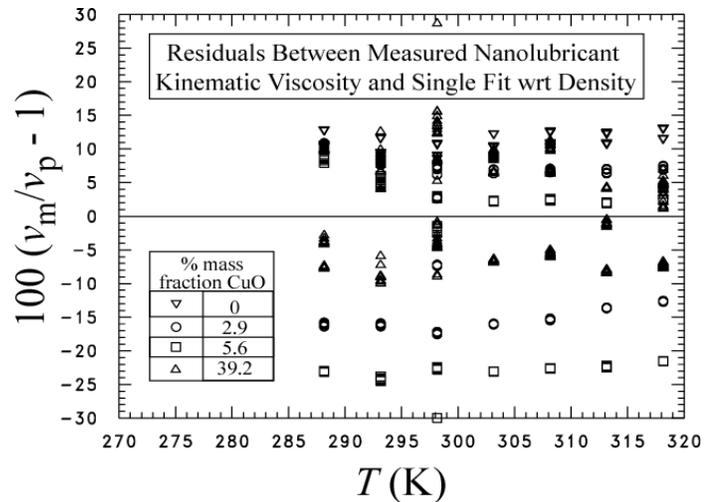

Figure 4 Residuals between measured nanolubricant kinematic viscosity and single fit with respect to liquid density

6. CONCLUSIONS

Liquid kinematic viscosity and liquid density measurements of a synthetic polyolester based copper (II) oxide (CuO) nanoparticle dispersion (nanolubricant) have been presented at atmospheric pressure and for a temperature range from approximately 288 K to 318 K. The CuO particles were approximately 30 nm-diameter, spherical, and well dispersed in the commercially available polyolester chiller lubricant. Viscosity and density measurements were made for the pure base lubricant along with three nanolubricants with differing CuO nanoparticle mass fractions (2.9 %, 5.6 % and 39.2 %). The Stokes-Einstein equation failed to predict the viscosity of the nanolubricant with the largest nanoparticle concentration. For this reason, the liquid kinematic viscosity was correlated with respect to liquid density and temperature. The viscosity of the nanolubricant increased with respect to its density and decreased with respect to its temperature. A linear relationship was developed for liquid specific volume with respect to temperature. The liquid density decreased with respect to temperature and increases with respect to the CuO mass fraction for the temperature range of the study.

ACKNOWLEDGEMENTS

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[4] Prasher et al. (2006) also found that the Einstein equation did not adequately predict the viscosity of propylene glycol and ethylene glycol based nanofluids.

this manuscript. The Stabinger Viscometer was operated by Mr. David Wilmering of KT Consultants at the NIST laboratory. The nanolubricant was manufactured by Nanophase Technologies with a copper (II) oxide and dispersant in RL68H especially for NIST.

NOMENCLATURE

A_n constants in Table 3 n=0,1,2,3
B_n constants in Table 2 n=0,1,2,3
T absolute fluid temperature (K)
T_r T/273.15 K (-)
ρ liquid density (kg·m^{-3})
ρ_L pu9re lubricant density (kg·m^{-3})
ρ_m measured liquid density (kg·m^{-3})

ρ_p predicted liquid density (kg·m^{-3})
ρ_s CuO nanoparticle density (kg·m^{-3})
ν liquid kinematic viscosity (mm^2·s^{-1})
ν_m measured liquid viscosity (mm^2·s^{-1})
ν_p predicted liquid viscosity (mm^2·s^{-1})
ν_o unity viscosity = 1 (mm^2·s^{-1})
x_m CuO mass fraction (-)

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