

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. The density of the CuO nanoparticles was shown to differ significantly from the known density for “macro” CuO. Viscosity and density measurements were made for the pure base lubricant along with three nanolubricants with differing nanoparticle volume fractions (2%, 4% and 40%). The viscosity and the density were shown to increase with respect to increasing nanoparticle volume 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 % results in the nanofluid having a thermal conductivity that was more than 40 % greater than that of the pure base fluid. Herein lies what is believed to be a great potential for the enhancement of liquid heat transfer by the addition of nanoparticles to the base fluids such as lubricants, i.e., nanolubricant.

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 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 $72.3 \text{ mm}^2 \cdot \text{s}^{-1}$ at 313.15 K was the base lubricant that was

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.

mixed with nominally 30 nm diameter copper (II) oxide (CuO) nanoparticles. Copper (II) oxide (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 40 % of the volume was CuO particles, which corresponds to a 0.603 mass CuO mass fraction. The mixture was diluted in-house to a 2 % and a 4 % volume fraction of CuO (0.044 and 0.087 mass CuO mass fraction, respectively) 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 used 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 manufacturer quoted uncertainty for the 95 % confidence level for the kinematic viscosity and the density was $\pm 0.35\%$ and $\pm 0.5 \text{ kg}\cdot\text{m}^{-3}$, 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 $1320 \text{ mm}^2\cdot\text{s}^{-1}$ and $845.4 \text{ kg}\cdot\text{m}^{-3}$, respectively. Residuals between the measurements and the calibration standard for 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 volume 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 $\pm 0.01\%$ and $\pm 2\%$, respectively. Adding CuO nanoparticles results in larger increases in the viscosity uncertainty than in the uncertainty of the density. For all of the nanolubricants, the uncertainty for the density and viscosity measurements were less than $\pm 0.5\%$, and $\pm 30\%$, respectively. The maximum uncertainty of the composition measurement is approximately 0.02 %, e.g., the range of a 2.0 % composition is between 1.98 % and 2.02 %. 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	RL68H2CuO	RL68H4CuO	RL68H40CuO
Viscosity ($\text{mm}^2\cdot\text{s}^{-1}$)	± 2 (± 2 %)	± 25 (± 20 %)	± 36 (± 30 %)	± 69 (± 13 %)
Density ($\text{kg}\cdot\text{m}^{-3}$)	± 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 volume fraction of the CuO nanoparticles being $\pm 0.03 \text{ kg}\cdot\text{m}^{-3}$, $\pm 0.05 \text{ kg}\cdot\text{m}^{-3}$, $\pm 0.10 \text{ kg}\cdot\text{m}^{-3}$, and $\pm 1.7 \text{ kg}\cdot\text{m}^{-3}$ for the 0 %, 2 %, 4 %, and the 40 % volume fraction nanolubricants, respectively.

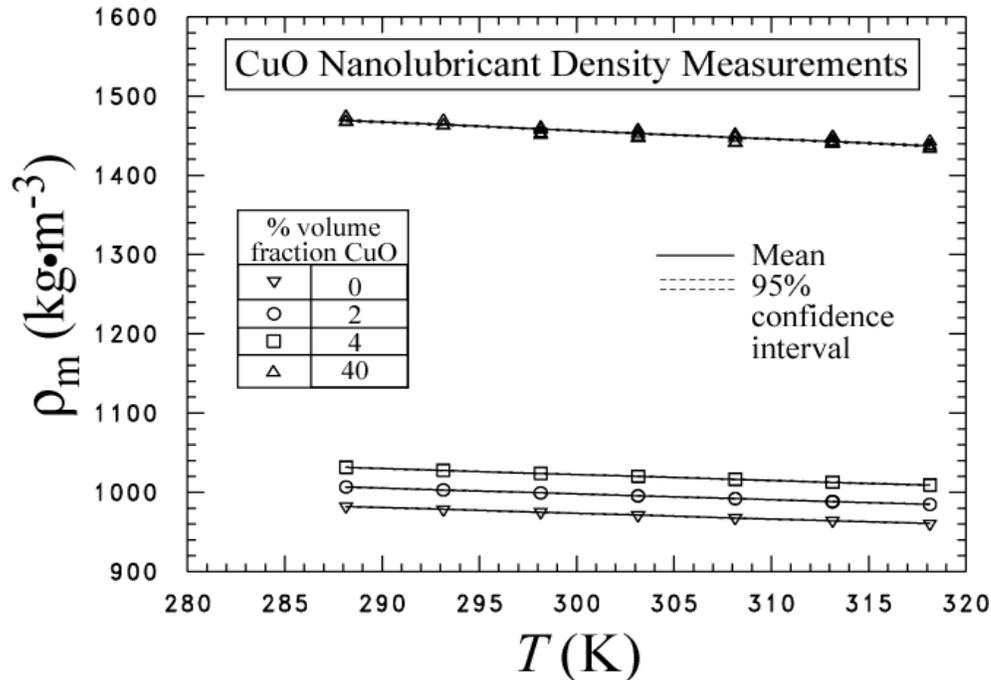


Figure 1 Measured liquid density of CuO nanolubricant for various volume fractions at atmospheric pressure

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

Fitting Constant	RL68H	RL68H2CuO	RL68H4CuO	RL68H40CuO
B_0	0.797907E-03	0.779375E-03	0.761094E-03	0.536832E-03
B_1	0.764702E-06	0.742542E-06	0.723165E-06	0.499238E-06

Figure 2 shows deviation between the measured density and the linear fits of the specific volume 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 volume fraction being $\pm 0.02\%$, $\pm 0.03\%$, and $\pm 0.04\%$ for the 0%, 2%, and 4% volume fractions, respectively. As explained above, the variation is likely due to small variations in the volume fraction that occurred between measurement runs with larger variations occurring at larger volume 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 agreement to within $\pm 0.02\%$ at 297.15 K when a CuO density of $2183 \text{ kg} \cdot \text{m}^{-3}$ (Kedzierski and Gong, 2007) is used for the density of the solid nanoparticles (ρ_s) along with the correlated density values for the pure lubricant (ρ_L). The same agreement can be achieved for the

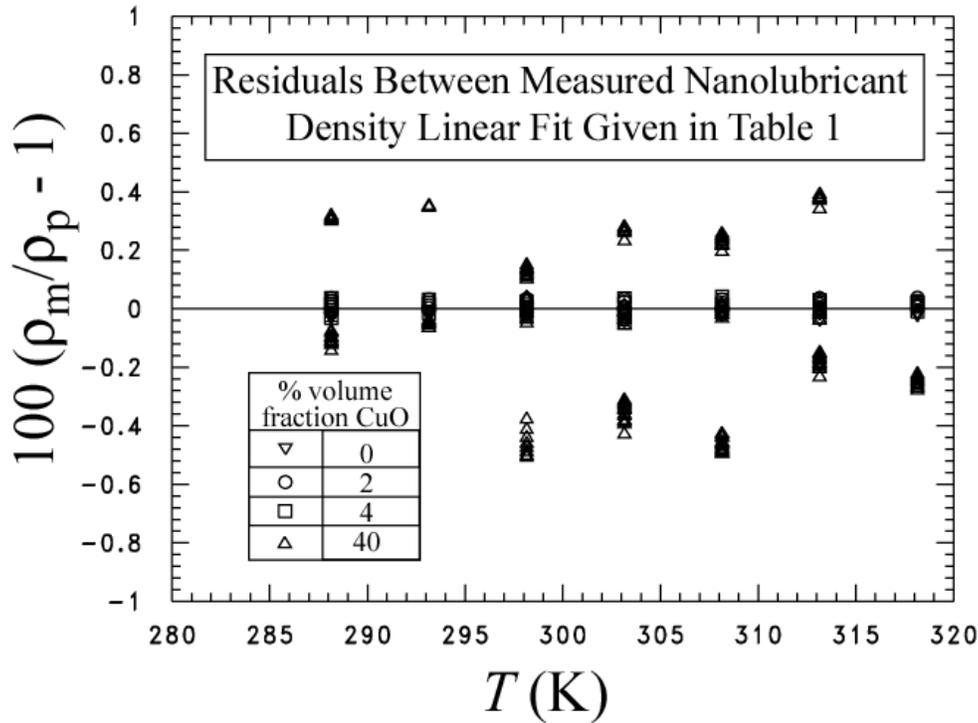


Figure 2 Residuals between measured nanolubricant density and linear fit of specific volume for all test fluids

entire temperature range (288 K to 319 K) when Eq. (1) is used to solve for the density of the CuO nanoparticles as a function of temperature:

$$\frac{1}{\rho_s} [\text{kg}^{-1} \cdot \text{m}^3] = 3.753 \times 10^{-4} + 2.797 \times 10^{-7} T [\text{K}] \quad (2)$$

Here the density has units of $\text{kg} \cdot \text{m}^{-3}$ while the input temperature has units of kelvin. Equation (2) has an uncertainty of $\pm 2\%$ and reproduces the Kedzierski and Gong (2007) to within 0.07%. However, Eq. (2) differs from the value of density given for “macro” CuO at room temperature² by nearly 200%: $6310 \text{ kg} \cdot \text{m}^{-3}$. This phenomenon where fundamental properties including density are size dependent on the nanoscale is well known and studied (Grassian, 2008 and Jamison et al., 2008).

4.2 Viscosity Measurements

Figure 3 shows the measured kinematic viscosity (ν) 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 (ν/ν_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):

$$\frac{\nu}{\nu_0} = \exp\left(A_0 + \frac{A_1}{T_r} + A_2 \ln(T_r) + A_3 T_r^{A_4}\right) \quad (3)$$

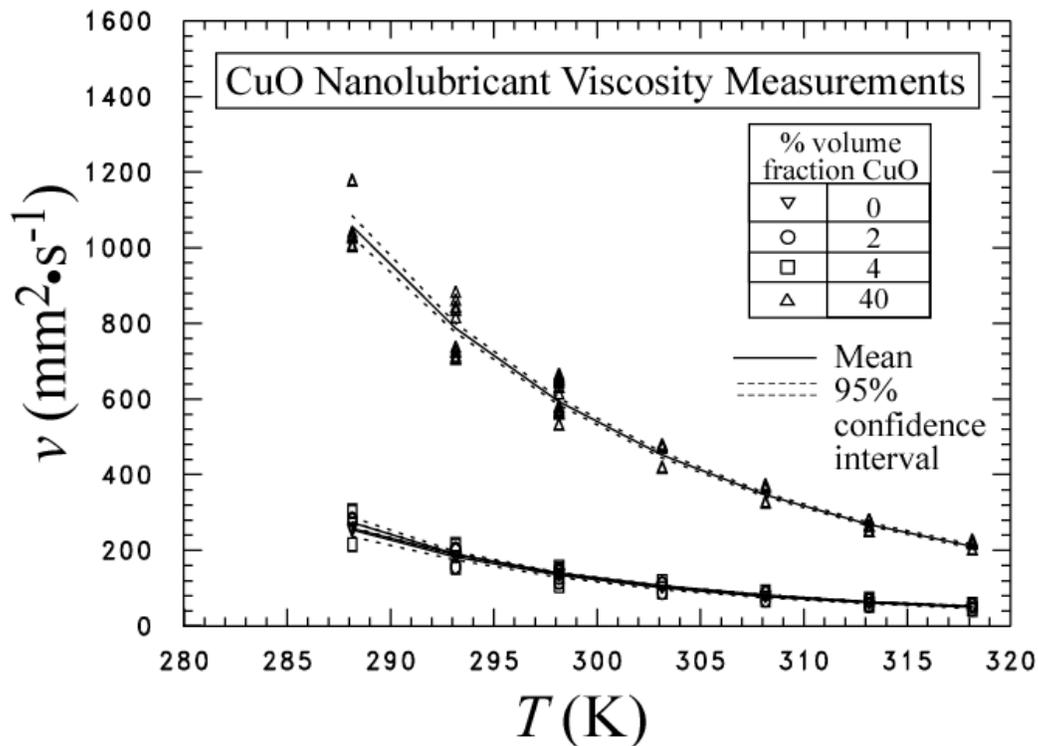


Figure 3 Measured liquid viscosity of CuO nanolubricant for various volume fractions at atmospheric pressure

² <http://www.nationmaster.com/encyclopedia/Copper%28II%29-oxide>

where ν_0 is the unity-viscosity ($\nu_0 = 1 \text{ mm}^2 \cdot \text{s}^{-1}$), 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, five of the 243 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. (3) 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 viscosity for the 95 % confidence level was shown to increase with respect to the volume fraction of the CuO nanoparticles being $\pm 0.5 \text{ mm}^2 \cdot \text{s}^{-1}$, $\pm 3.9 \text{ mm}^2 \cdot \text{s}^{-1}$, $\pm 6.7 \text{ mm}^2 \cdot \text{s}^{-1}$, and $\pm 10.2 \text{ mm}^2 \cdot \text{s}^{-1}$ for the 0 %, 2 %, 4 %, and the 40 % volume fraction nanolubricants, respectively. The residuals for the fits given in Table 3 are within $\pm 15 \%$ for all of the fluids. Although the relative percent residuals did not increase with respect to volume fraction, the absolute residuals did.

Table 3. Viscosity fit with respect to temperature: $\frac{\nu}{\nu_0} = \exp\left(A_0 + \frac{A_1}{T_r} + A_2 \ln T_r\right)$

Fitting Constant	RL68H	RL68H2CuO	RL68H4CuO	RL68H40CuO
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

Correlation of the density and the viscosity with respect to CuO mass fraction (x_m) or density produced a significantly better fit than doing so with respect to volume fraction. The following section presents the results of these correlations.

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:

$$\frac{1}{\rho} [\text{kg}^{-1} \cdot \text{m}^3] = (7.626 \times 10^{-7} - 4.373 \times 10^{-7} x_m) T [\text{K}] + 7.984 \times 10^{-4} - 4.337 \times 10^{-4} x_m \quad (4)$$

where the density (ρ) has units of $\text{kg} \cdot \text{m}^{-3}$ while the input temperature (T) has units of kelvin. Equation (4) 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 $\pm 0.02 \%$, $\pm 0.03 \%$, $\pm 0.04 \%$, and $\pm 0.6 \%$ for the 0 %, 2 %, 4 %, and 40 % volume fractions, respectively. Consistent with Eq. (1), Eq. (4) shows that the liquid density of the nanolubricant increases linearly with increasing CuO mass fraction.

5.2 Viscosity

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

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

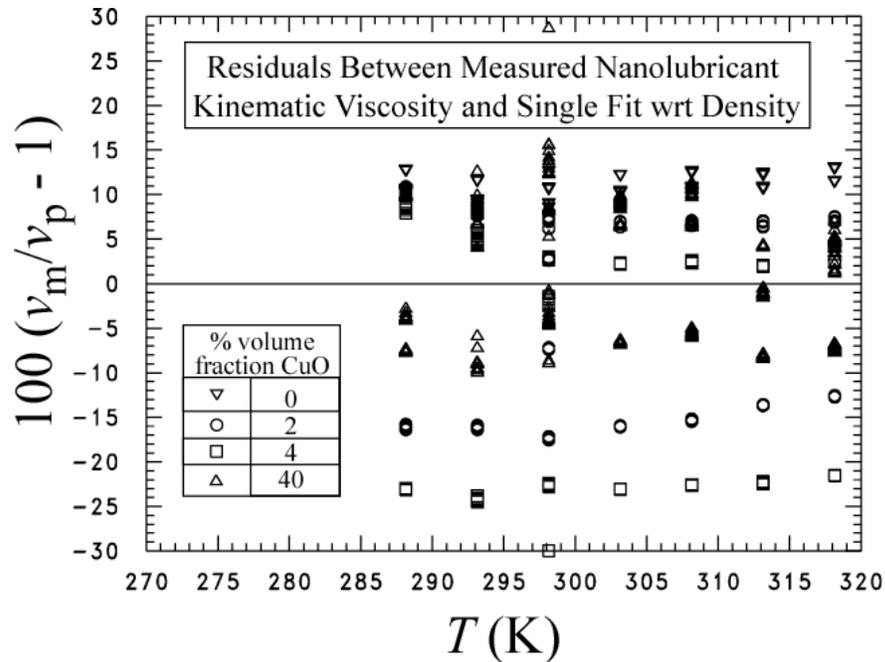


Figure 4 Residuals between measured nanolubricant kinematic viscosity and single fit with respect to liquid density

increasing density, i.e., increasing nanoparticle volume fraction.

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. In addition, the density of the CuO nanoparticles was calculated from the measurements as a function of temperature and shown to be nearly 200 % less than the known macro density of CuO. 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 volume fractions (2%, 4% and 40%). 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 density. The liquid density decreased with respect to temperature and increases with respect to the CuO mass fraction for the temperature range of the study.

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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. (4) and used as input for Eq. (5). Figure 4 shows that 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

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 ($\text{kg}\cdot\text{m}^{-3}$) ρ_L pure lubricant density ($\text{kg}\cdot\text{m}^{-3}$) ρ_m measured liquid density ($\text{kg}\cdot\text{m}^{-3}$)	ρ_p predicted liquid density ($\text{kg}\cdot\text{m}^{-3}$) ρ_s CuO nanoparticle density ($\text{kg}\cdot\text{m}^{-3}$) ν liquid kinematic viscosity ($\text{mm}^2\cdot\text{s}^{-1}$) ν_m measured liquid viscosity ($\text{mm}^2\cdot\text{s}^{-1}$) ν_p predicted liquid viscosity ($\text{mm}^2\cdot\text{s}^{-1}$) ν_o unity viscosity = 1 ($\text{mm}^2\cdot\text{s}^{-1}$) x_m CuO mass fraction (-)
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