Formula for the Viscosity of a Glycerol-Water Mixture

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An empirical formula is proposed for the calculation of the viscosity of glycerol—water mixture for mass concentrations in the range of 0-100% and temperatures varying from 0 to 100 °C. It compares well with three databases available in the literature, and its application procedure is also simpler than other previously developed correlations.

Introduction

Many industrial applications require knowledge of liquid viscosities, for example, for optimizing chemical processes and determining power supplies associated with pipeline transportation and pump operations. Aqueous glycerol solutions are widely used in experimental studies of flow phenomena. Experiments conducted with glycerol solutions facilitate investigation of flows in a wide range of Reynolds numbers. However, the approach used to estimate the viscosity of glycerol solutions is still incomplete in the literature. This is largely because there is no comprehensive theory on the viscosity of liquids at present. Some theoretical approaches including those developed on the basis of molecular dynamics could provide valuable understandings of relevant fundamentals but often cause large deviations from measured viscosity data.^{1,2}

Practically, calculation of the mixture viscosity is often performed with empirical data-driven correlations between viscosity and other liquid properties. Such correlations are generally interpolative. Some are simple but applicable to limited conditions, while the others may involve application procedures that are tedious. For example, Chen and Pearlstein proposed a four-parameter correlation for the dynamic viscosity (μ) of glycerol—water mixtures

$$\mu = A_1 \exp[A_2(T + 273.15)^{-3} + A_3(T + 273.15) + A_4(T + 273.15)^{-1}]$$
 (1)

where μ is in cP or 0.001 Ns/m², T is in °C, and the coefficients, A_1 – A_4 , vary with the glycerol concentration in mass ($C_{\rm m}$). Use of eq 1 is restricted because the values of A_1 – A_4 are only given for some discrete concentrations, i.e., $C_{\rm m} = 40\%$, 50%, ..., 90%, 99%, 100%. For other concentrations, numerical interpolations or extrapolations are necessary, which may induce additional computational errors.

Shankar and Kumar⁴ suggested the kinematic viscosity (ν) of aqueous glycerol solutions be estimated as

$$\frac{\ln(\nu/\nu_{\rm w})}{\ln(\nu_{\rm g}/\nu_{\rm w})} = C_{\rm m}[1 + (1 - C_{\rm m})(B_1 + B_2C_{\rm m} + B_3C_{\rm m}^2)]$$
 (2)

where subscripts g and w denote glycerol and water, respectively, and B_1 – B_3 are the temperature-dependent coefficients. Similar difficulties are encountered in applying eq 2 because the B coefficients were evaluated only for five discrete temperatures, i.e., T=10, 20, 30, 40, and 50 °C.

A recent effort for determining kinematic viscosities of glycerol solutions was made by Chenlo et al.⁵ They related the kinematic viscosity to the mole fraction of glycerol ($C_{\rm mol}$) and temperature, i.e.

$$\frac{\nu}{\nu_{\rm w}} = 1 + 0.125 C_{\rm mol} \exp\left(\frac{C_{\rm mol}^{0.219}}{2.291[(T + 273.1)/273.1]^3 - 1}\right)$$
(3)

where $\nu_{\rm w}$ (m²/s) is given by

$$\nu_{\rm w} = 0.09607 \times 10^{-6} \exp\left(\frac{2.9}{[(T + 273.1)/273.1]^3}\right)$$
 (4)

Equation 3 does not engage any unknown coefficients and also reproduces Chenlo et al.'s data with small deviations. However, it cannot be applied for high glycerol concentrations. For example, when compared with the data by Shankar and Kumar,⁴ eq 3 yields significant deviations, which reach up to 9% for $C_{\rm m}=40\%$ and 50% for $C_{\rm m}=70\%$.

In this study, a formula for the dynamic viscosity of glycerol—water mixtures is proposed, which is applicable for a wide variety of conditions, i.e., $C_{\rm m}=0-100\%$ and T=0-100 °C. Comparisons are also made between the proposed formula and three different sets of experimental data available in the literature.

Formulation Proposed in this Study

In the following, the analysis is conducted for temperatures varying from 0 to 100 °C at atmospheric pressure. First, the dynamic viscosity of the glycerol—water mixture, μ , is related to those of the two components in the power form

$$\mu = \mu_{\rm w}^{\alpha} \mu_{\rm g}^{1-\alpha} \tag{5}$$

where subscripts w and g denote water and glycerol, respectively, and α is the weighting factor varying from 0 to 1. Equation 5 can be also rewritten as

$$\mu = \mu_{\sigma} \exp(A\alpha) \tag{6}$$

where $A = \ln(\mu_{\rm w}/\mu_{\rm g})$. Equation 6, in its exponential form, resembles eqs 1 and 2. Other formulas similar to eq 5 were also reported previously, but the weighting factors involved were only associated with the concentration of glycerol. Actually, as shown later, α varies with temperature as well as concentration.

With eq 5, α is given by

$$\alpha = \frac{\ln(\mu/\mu_{\rm g})}{\ln(\mu_{\rm w}/\mu_{\rm g})} \tag{7}$$

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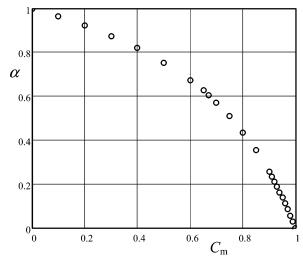


Figure 1. Dependence of α on glycerol concentration in mass at T = 20 °C. Data are taken from Segur and Oberstar.⁶

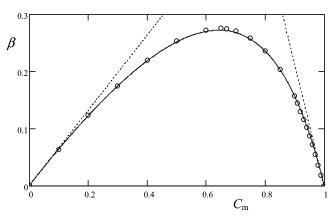


Figure 2. Relation of β – $C_{\rm m}$ at T = 20 °C in comparison with interpolating function. Data are taken from Segur and Oberstar.⁶

Equation 7 predicts that α decreases from 1 to 0 with increasing concentration, as implied by experimental data. This is illustrated in Figure 1 for T=20 °C with the data given by Segur and Oberstar.⁶

To examine the variation of α in detail, the above graph is re-plotted in Figure 2 as β (= α - 1 + $C_{\rm m}$) against $C_{\rm m}$. Figure 2 shows that β varies almost linearly as $C_{\rm m}$ approaches 0% and 100%. These linear variations are approximated as follows

$$\beta_1 = aC_{\rm m} \text{ for } C_{\rm m} \to 0 \tag{8}$$

$$\beta_2 = b(1 - C_{\rm m}) \text{ for } C_{\rm m} \to 100\%$$
 (9)

To estimate the nonlinear change in β for $0 < C_{\rm m} < 100\%$, a power-sum interpolating function is applied here

$$\beta^n = \beta_1^n + \beta_2^n \tag{10}$$

where n is an exponent. The best fit using eq 10 is almost achieved with n=-1, as shown in Figure 2. For experimental data collected for other temperatures between 0 and 100 °C, 6 eq 10 with n=-1 can also provide similar approximations. Substituting eqs 8 and 9 into eq 10 and noting that $\alpha=1-C_{\rm m}+\beta$, we get

$$\alpha = 1 - C_{\rm m} + \frac{abC_{\rm m}(1 - C_{\rm m})}{aC_{\rm m} + b(1 - C_{\rm m})}$$
(11)

Evaluation of Coefficients a and b

To estimate a and b, the data used are those collected by Segur and Oberstar⁶ for $0 \, ^{\circ}\text{C} < T < 100 \, ^{\circ}\text{C}$. The relations of

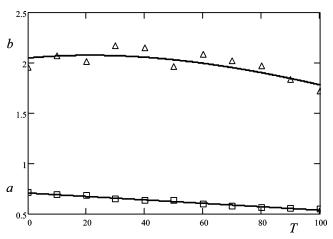


Figure 3. Variations of a and b with temperature, T (°C). The symbols denote the values estimated from the data by Segur and Oberstar.⁶

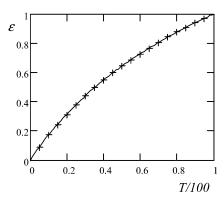


Figure 4. Variation of ϵ with T/100 for water. T is in °C. Data are taken from Washburn et al.⁷

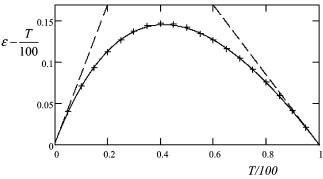


Figure 5. Variation of ϵ –T/100 with T/100 in comparison with interpolating function denoted by solid line. T is in °C. The dash lines represent linear asymptotes. Data are taken from Washburn et al.⁷

a and b to the temperature are shown in Figure 3, which are further approximated by

$$a = 0.705 - 0.0017T \tag{12}$$

$$b = (4.9 + 0.036T)a^{2.5} (13)$$

Evaluations of $\mu_{\rm w}$ and $\mu_{\rm g}$

The proposed formula, eq 5, is interpolative in nature, so the viscosities of the two components, $\mu_{\rm w}$ and $\mu_{\rm g}$, must be known.

Dynamic Viscosity of Water, $\mu_{\rm w}$. It is noted that $\mu_{\rm w}$ generally reduces with increasing temperature, T. The reduction can be presented in the form similar to eq 5

$$\mu_{\mathbf{w}} = \mu_{\mathbf{w}100}^{\epsilon} \mu_{\mathbf{w}0}^{1-\epsilon} \tag{14}$$

where $\mu_{\rm w0}$ is the dynamic viscosity at T=0 °C, $\mu_{\rm w100}$ is that at T=100 °C, and ϵ is the weighting factor in the range 0–1. From eq 14

$$\epsilon = \frac{\ln(\mu_{\rm w}/\mu_{\rm w0})}{\ln(\mu_{\rm w100}/\mu_{\rm w0})}$$
 (15)

With the data by Washburn et al.,⁷ the variation of ϵ with T/100 is computed and plotted in Figure 4. It can be observed that the variations at T approaching 0 and 100 °C are approximately linear. Therefore, it is assumed that

$$\epsilon = a_{\rm w} \left(\frac{T}{100} \right)$$
 for $T \to 0$ °C (16)

$$1 - \epsilon = b_{\rm w} \left(1 - \frac{T}{100} \right) \text{ for } T \to 100 \,^{\circ}\text{C}$$
 (17)

where $a_{\rm w}$ and $b_{\rm w}$ are coefficients. Equations 16 and 17 can be also transformed to

$$\epsilon - \frac{T}{100} = (a_{\rm w} - 1) \left(\frac{T}{100}\right) \text{ for } T \to 0 \text{ °C}$$
 (18)

$$\epsilon - \frac{T}{100} = (b_{\rm w} - 1)(\frac{T}{100} - 1) \text{ for } T \to 100 \,^{\circ}\text{C}$$
 (19)

It is proposed here that the above two equations be generalized for $0 \, ^{\circ}\text{C} < T < 100 \, ^{\circ}\text{C}$ as follows

$$\left(\epsilon - \frac{T}{100}\right)^{-1} = \left[(a_{\rm w} - 1) \left(\frac{T}{100} \right) \right]^{-1} + \left[(b_{\rm w} - 1) \left(\frac{T}{100} - 1 \right) \right]^{-1}$$
 (20)

Equation 20 is plotted in Figure 5, showing that the interpolating function is generally close to the data points reported by Washburn et al.⁷ It is noted that the interpolating technique is the same as that used in eq 10 and Figure 2.

Solving for ϵ from eq 20 and substituting into eq 14 yields

$$\mu_w = 1.790 \exp\left(\frac{(-1230 - T)T}{36100 + 360T}\right)$$
 (21)

where μ_w is in cP or 0.001 Ns/m², T is in the range of 0–100 °C, and the four constants are estimated by applying the data given by Washburn et al. Equation 21 represents the Washburn et al. Additional calculations show that eq 21 can also reproduce the data reported by Linstrom and Mallard with deviations less than 0.5%.

Dynamic Viscosity of Glycerol, μ_{g} . Similarly, the following exponential formula is proposed for calculating the dynamic viscosity of glycerol

$$\mu_{\rm g} = 12\ 100\ \exp\left(\frac{(-1233 + T)T}{9900 + 70T}\right)$$
 (22)

where $\mu_{\rm g}$ is in cP or 0.001 Ns/m² and *T* is in °C. Equation 22 is calibrated using the data, which were given by Segur and Oberstar⁶ for $T = 0{-}100$ °C, with differences being less than

3%. In addition, eq 22 also compares well with the following five-parameter fit by Stengel et al.⁹

$$v_{\rm g} = \exp(4.549 - 0.12309T + 9.1129 \times 10^{-4}T^2 - 4.7562 \times 10^{-6}T^3 + 1.3296 \times 10^{-8}T^4)$$
 (23)

where ν_g is in cm²/s. To convert ν_g to μ_g , the glycerol density, ρ_g (kg/m³), is computed as

$$\rho_{\rm g} = 1277 - 0.654T \tag{24}$$

which gives the best fit of the measurements for T = 17-83 °C by Adamenko et al.¹⁰ The predicted dynamic viscosities using eqs 22 and 23 differ at most by 1.6%.

Comparisons and Discussions

Three databases are used for comparison purposes, as summarized in Table 1. The first one was provided by Segur and Oberstar,⁶ with which the two coefficients, *a* and *b*, used for eq 5 are evaluated. The other two databases available in the literature are due to Shankar and Kumar⁴ and Chenlo et al.,⁵ respectively. Differences between the formula predictions and these databases are examined in this section.

Shankar and Kumar⁴ measured the kinematic viscosity of glycerol—water solutions for glycerol mass fractions in the range $C_{\rm m}=0{-}100\%$ in the temperature range of $10{-}50$ °C. Chenlo et al.'s data were collected in the glycerol fraction of $C_{\rm mol}=0{-}5$ mol (per kg of water) or $C_{\rm m}=0{-}31.5\%$ at temperatures from 20 to 50 °C. The glycerol concentration in mass ($C_{\rm m}$) is related to the fraction in mol ($C_{\rm mol}$) as $C_{\rm m}=M_{\rm g}C_{\rm mol}/(1000+M_{\rm g}C_{\rm mol})$, where $M_{\rm g}$ is the molecular weight of glycerol (=92.09 g). To make conversion between μ and ν , the density of the mixture (ρ) is calculated approximately as

$$\rho = \rho_{\rm g} C_{\rm m} + \rho_{\rm w} (1 - C_{\rm m}) \tag{25}$$

where $\rho_{\rm g}$ is the glycerol density and $\rho_{\rm w}$ is the water density. Theoretically, eq 25 is considered inexact because of possible interactions of the two components. However, the error induced is generally very small. It varies within $\pm 0.8\%$ on the basis of the data provided by Adamenko et al., ¹⁰ who measured the mixture density for the condition of T=17-83 °C and $C_{\rm m}=60-86\%$. In eq 25, $\rho_{\rm g}$ is computed using eq 24, and $\rho_{\rm w}$ is computed with the empirical formula proposed as follows

$$\rho_{\rm w} = 1000 \left(1 - \left| \frac{T - 4}{622} \right|^{1.7} \right) \tag{26}$$

where $\rho_{\rm w}$ is in kg/m³ and T is in °C. Equation 26 predicts the water density for T=0-100 °C with errors less than 0.02%, when compared with the data by Linstrom and Mallard.⁸

The computed dynamic viscosities are plotted in Figure 6, which simulates well all three databases. To further assess the

Table 1. Summary of Experimental Data Used for Comparisons

databases	range of T (°C)	range of $C_{\rm m}$ (%)	maximum prediction error (%)	average prediction error (%)	number of data points predicted with error		
					>5%	<5%	<3%
Segur and Oberstar ⁶ Shankar and Kumar ⁴ Chenlo et al. ⁵	0-100 10-50 20-50	0-100 0-100 0-31.5	3.5 8.5 2.2	1.3 2.3 0.7	0 6 0	256 102 42	246 79 42

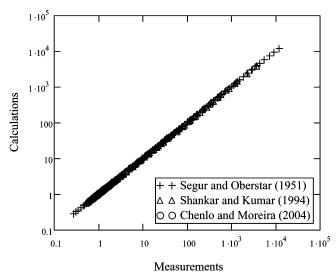


Figure 6. Calculated dynamic viscosities in comparison with measurements. The unit is cP.

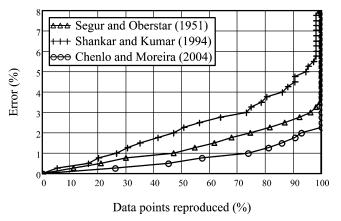


Figure 7. Percentage of data points reproduced and associated predicting error.

predictions using the present approach, the predicting error for each data point is calculated as

$$\mathrm{Error}(\%\) = \frac{|\mu_{\mathrm{calculated}} - \mu_{\mathrm{measured}}|}{\mu_{\mathrm{measured}}} \times 100$$

As summarized in Table 1, among more than 400 data points, only six are predicted with errors greater than 5%. The maximum prediction error is 3.5%, 8.5%, and 2.2% for the databases given by Segur and Oberstar, ⁶ Shankar and Kumar, ⁴ and Chenlo et al., ⁵ respectively, while the average error reduces to 1.3%, 2.3%, and 0.7%, respectively. In Figure 7, the

percentage of data points reproduced is plotted against the associated maximum error, Error(%). It shows that the predicting errors using the proposed approach are generally small. For example, to reproduce 95% of the data points, the maximum error induced is about 2% for the measurements by Chenlo et al., 5 3% for those by Segur and Oberstar, 6 and 5% for those by Shankar and Kumar. 4

Conclusions

An exponential formula is developed in this study to calculate the viscosity of a glycerol—water mixture. A power-sum interpolating function is employed to evaluate factors involved. The derived formula applies for glycerol concentration in mass in the range of 0-100% and temperatures varying from 0 to 100 °C. It is simple to use, in comparison with similar relations developed previously, and able to reproduce 95% of measured viscosities from the three databases with deviations less than 5%.

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