



Density model for aqueous glycerol solutions

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Abstract

Glycerol is used in many applications of science and daily life as it is cheap and biologically non-invasive. In science, aqueous solutions of glycerol are commonly used for experimental investigations as their density can be adapted by changing the glycerol content in the solution. Although the density of aqueous glycerol solutions has been measured precisely since more than a century, current models show a deviation from measured data of up to 2%. In this work we present an analytical expression to accurately calculate the density of aqueous glycerol solutions. The presented empirical model is validated in the range between 15 and 30 °C and has a maximum deviation of less than 0.07% with respect to measured data. This improves the accuracy of current models by more than one order of magnitude. By knowing the temperature and glycerol content of the solution, its density can be simply calculated with the presented model. A Matlab function is provided in the supplementary material to allow a simple implementation in other scientific work.

1 Introduction

Glycerol is used in many applications within the scientific fields of fluid mechanics, chemistry, medicine, and biology. In daily life glycerol is commonly used in pharmaceutical and personal care products, as well as an anti-freeze and in food industry, because it is cheap and non-toxic (Ayoub and Abdullah 2012). In scientific work the exact determination of the density of aqueous glycerol solutions is important. By mixing glycerol with water, the density of the solution at room temperature can be adapted in the range from 1000 kg/m³ (pure water) to 1260 kg/m³ (pure glycerol). This possibility of adapting the liquid density is why glycerol is used in many scientific fields in particular in fluid mechanics and biotechnology. A specific example for the application of this technique in fluid mechanics is the matching of the liquid density to polymer particles, which allows them to follow the streamlines. This property can be used in measurement technologies to determine the structure of a flow

field (Adrian and Westerweel 2011; Raffel et al. 2018). In biotechnology, glycerol density gradients allow to separate biological material by centrifugation (Hansen et al. 1987). Due to the various applications mentioned above, densities of aqueous glycerol solutions have been measured since more than a century. Whereas first measurements by Gerlach (1884) and Strohmer and Gerlach (1885) were accurate to four significant digits, several detailed investigations on the properties of aqueous glycerol solutions have been published later in the early 20th century by Washburn and West (1926) and Timmermans (1935), as well as by Bosart and Snoddy (1927) and Bosart and Snoddy (1928) and determined the density of glycerol and its aqueous solution with a precision up to five significant digits. A summary of tables on glycerol measurements can be found in a publication by the Glycerine Producers' Association (1963). On the other hand, a precise formula to calculate the density based on temperature and glycerol content has not yet been presented. An attempt to summarize these measurements in a formula has been presented by Cheng (2008). However, in that work, the density of the solution is wrongly calculated using the mass fractions of the solutes instead of the volume fractions. Moreover the effect of volume contraction is not taken into account. In the work presented here, these aspects are corrected to develop a model for the density of aqueous glycerol solutions that precisely fits with the measured data of Bosart and Snoddy (1928).

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2 Density relation for aqueous glycerol solutions

Assuming an ideal solution, its density ρ_s is given by

$$\rho_s(T, \phi_i) = \sum_{i=1}^N \rho_i(T) \phi_i, \quad (1)$$

where N is the number of components, T the temperature value in °C, ϕ_i the volume fraction of the i th component, and $\rho_i(T)$ its temperature-dependent density. However, Eq. (1) does not take into account the volume contraction, an effect that is typically small but occurs for most liquid mixtures and leads to a solution volume V_s that is smaller than the sum of the component volumes $\sum_i V_i$ (Prigogine et al. 1957). To set up a model with high accuracy, this effect is also taken into account in this work. Thus, the volume contraction coefficient κ is introduced as the ratio:

$$\kappa = \frac{1}{V_s} \sum_i V_i. \quad (2)$$

By analyzing measured data of aqueous glycerol solutions, it can be found that κ not only depends on the volume fraction of glycerol, but also on the temperature of the solution (Bosart and Snoddy 1928). With the volume contraction the density of an aqueous glycerol solution is given by

$$\rho_s(T, \phi_g) = \kappa(T, \phi_g) [\rho_g(T)\phi_g + \rho_0(T)(1 - \phi_g)], \quad (3)$$

where ϕ_0 and ϕ_g are the volume fractions of water and glycerol and $\rho_0(T)$ and $\rho_g(T)$ the densities, respectively. As the mass fraction w_i is more commonly used than the volume fraction ϕ_i to describe the amount of the components in a solution, the conversion:

$$\phi_g = \left[1 + \frac{\rho_g(T)}{\rho_0(T)} \left(\frac{1}{w_g} - 1 \right) \right]^{-1} \quad (4)$$

is used in the following. The resulting expression for the density of an aqueous glycerol solution is then

$$\rho_s(T, w_g) = \kappa(T, w_g) \left[\rho_0(T) + \frac{\rho_g(T) - \rho_0(T)}{1 + \frac{\rho_g(T)}{\rho_0(T)} \left(\frac{1}{w_g} - 1 \right)} \right]. \quad (5)$$

3 Model for the density of aqueous glycerol solutions

The model presented in this work is based on experimental data which is shown in Table 1 of the supplementary material where the density of aqueous glycerol solutions

ρ_s was measured by Bosart and Snoddy in a temperature range between 15 and 30 °C for glycerol weight fractions between 0 and 100% with an uncertainty $\Delta\rho_s \approx 0.1 \text{ kg/m}^3$ (Bosart and Snoddy 1928). Based on this data, a model will be developed in this work to describe the density of aqueous glycerol solutions. The model uses the density of pure water ρ_0 (Linstrom and Mallard 2005; Wagner and Pruß 2002) and pure glycerol ρ_g (Bosart and Snoddy 1928) to calculate ρ_s . The uncertainties of the measured densities of the pure components are $\Delta\rho_0 \approx 0.01 \text{ kg/m}^3$ and $\Delta\rho_g \approx 0.1 \text{ kg/m}^3$. With Eq. (2) and the given uncertainties, the uncertainty of the volume contraction coefficient is $\Delta\kappa \approx 0.0002$ according to linear error calculation.

The densities of the pure liquids can be approximated with the empirical expressions:

$$\rho_0(T) = 1000 \left(1 - \left| \frac{T - 3.98}{615} \right|^{1.71} \right) \frac{\text{kg}}{\text{m}^3} \quad (6)$$

for water and

$$\rho_g(T) = (1273 - 0.612 T) \frac{\text{kg}}{\text{m}^3} \quad (7)$$

for glycerol (adapted from Cheng (2008) to fit the data of Linstrom and Mallard (2005) and Bosart and Snoddy (1928), respectively). Equation 6 describes the temperature dependent density of water where the maximum deviation from the measured data is less than 0.3 kg/m^3 (0.03%) in the temperature range between 0 and 100 °C. For glycerol, the temperature dependent density is given by Eq. (7) and the maximum deviation from the measured data is less than 0.4 kg/m^3 (0.03%) in the temperature range between 15 and 30 °C. For pure liquids κ has to be exactly one. To guarantee this it can be approximated by the function

$$\kappa(T, w_g) = 1 + A \sin(w_g^{1.31} \pi)^{0.81}, \quad (8)$$

where A is the temperature dependent coefficient

$$A = 1.78 \times 10^{-6} T^2 - 1.82 \times 10^{-4} T + 1.41 \times 10^{-2}. \quad (9)$$

Equations (8) and (9) were determined based on the measurements of Bosart and Snoddy (1928). Figure 1 shows a comparison between κ calculated by the model given in Eq. (8) and the same coefficient determined based on the measured data as a function of glycerol content and temperature. The maximum deviation of κ from the measured data is 0.0004 which is only by a factor of 2 higher than the calculated uncertainty based on the measurements.

The density of aqueous glycerol solutions is calculated by substituting Eqs. (6)–(8) into Eq. (5). When

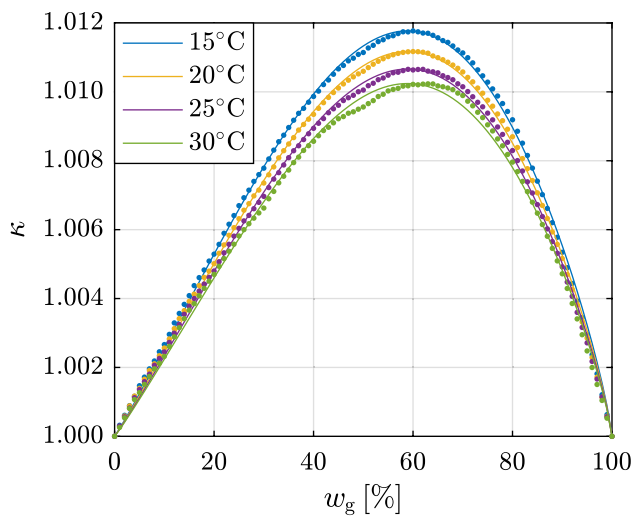


Fig. 1 Coefficient κ of aqueous glycerol solutions as a function of glycerol mass fraction w_g and Temperature T . Data points were calculated from the data of Bosart and Snoddy (1928) (dotted lines). Model for contraction is given by Eq. (8) (solid lines). The maximum deviation of the model from the measured data is approximately 0.0004. A maximum of the volume contraction can be observed for glycerol mass fractions of about 60%. With increasing temperature, κ is decreasing according to Eq. (9)

comparing the results with the measurements which are given in Bosart and Snoddy (1928) in the temperature range between 15 and 30 °C, the maximum deviation between model and measured data is less than 0.7 kg/m³ (0.07%). In comparison, the commonly used model of Cheng (2008), which does not take into account volume contraction shows a maximum deviation from measured data of about 2%. A more recent but less known work by Cristancho et al. (2011) is using the Jouyban–Acree model (Jouyban et al. 2004) to estimate the density of aqueous glycerol solutions and achieved results with a maximum deviation from measured data of about 0.4%. The model presented in this work is, therefore, strongly improving other density models of aqueous glycerol solutions and is much closer to the measurement uncertainty of 0.01%.

Figure 2 shows a comparison of the model presented in this work with the models of Cheng (2008) and Cristancho et al. (2011), respectively. The measured data of Bosart and Snoddy (1928) is also shown in the figure. To enable an easy implementation of the above results in other scientific work, a matlab function with the model is provided in the supplementary material. An online calculator for the density and viscosity of aqueous glycerol solutions is provided by Chris Westbrook (http://www.met.reading.ac.uk/~sws04cdw/viscosity_calc.html). The tables in the supplementary material show a comparison between the measured data (Supplementary Table 1) and the model (Supplementary Table 2) as well as calculated

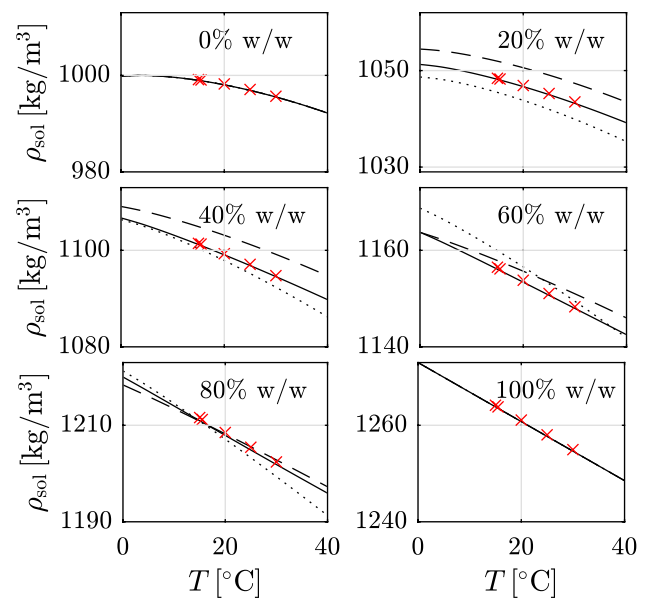


Fig. 2 Comparison between density measurements and analytical density models of aqueous glycerol solutions with various glycerol contents by weight (w/w). Solid lines represent the model given in Eq. (5), dashed lines the model of Cheng (2008), dotted lines the model of Cristancho et al. (2011), and the cross-markers the measured data by Bosart and Snoddy (1928). Comparing the models with experimental data in the temperature range between 15 and 30 °C, the models of Cheng and Cristancho et al. show a clear deviation of up to 2%. In contrast the model presented in this work that takes into account the volume contraction has a maximum deviation from the measured data of less than 0.07% and is much closer to the measurement error of 0.01%

densities of aqueous glycerol solutions at typical lab temperatures between 15 and 29 °C (Supplementary Tables 3, 4, 5).

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