

A Model for Predicting the Density of Glycerol Water Mixture, and Its Applicability to Other Alcohol Water Mixture

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Abstract

A mixture of alcohol and water is commonly used as antifreeze, liquor, and the fundamental solvents for the manufacture of cosmetics, pharmaceuticals, and inks in our daily life. Since various properties of alcohol water mixtures such as density, boiling or melting point, viscosity, and dielectric constant are determined by their mixing ratio, it is very important to know the mixing ratio to predict their properties. One of simple method to find the mixing ratio is measuring the density of the mixtures. However, it is not easy to predict the mixing ratio from the density of the mixtures because the relationship between mixing ratio and density has not been established well. The relationship is dependent on the relative sizes of solute and solvent molecules, and their interactions. Recently, an empirical model to predict the density of glycerol water mixture from their mixing ratio has been introduced. The suggested model is simple but quite accurate for glycerol water mixture. In this article, we investigated the applicability of this model to different alcohol water mixtures. Densities for six different alcohol water mixtures containing various alcohols (e.g., ethylene glycol, 1,3-propane diol, propylene glycol, methanol, ethanol, and 1-propanol) were simulated and compared to experimentally measured ones to investigate the applicability of the model proposed for glycerol water mixtures to other alcohol water mixtures. The model predicted the actual density of all alcohol water mixtures tested in this article with high accuracy at various ratios. This model can probably be used to predict the mixing ratio of other alcohol water mixtures from their densities beyond 6 alcohols tested in this article from their densities.

Keywords: Density, Alcohol, Binary Mixture, Model

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1. Introduction

A mixed solution of alcohol and water is a commonly used mixture in our daily life. For example, a mixture of ethylene glycol and water has been widely used as an antifreeze coolant in automobiles, and antifreeze concrete in constructions.^[1,2] As another example, a mixture of glycerol and water is usually used to manufacture cosmetics, pharmaceuticals, and inks, and an ethanol-water mixture is always produced in the process of making fermented liquor.^[3,4] In addition to these

examples, there are many more cases where a mixed solution consisting of various alcohols and water is used.^[5-7] Many physicochemical properties of the mixtures (e.g., density, boiling, and melting point) are determined by the mixing ratio of alcohol to water mixture. In addition, optical and electrical properties such as refractive index, and dielectric constants of the mixtures also depend on the mixing ratio.^[8] Also, the solubility for the same solute may differ depending on the mixing ratio. This is important property in practical point of view, because it is possible to extract a specific sub-

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stance more efficiently by changing the mixing ratio.^[9,10] Therefore, it is important to find out what the mixing ratio of the mixed solution is. If the relation between the mixing ratio and a particular property is well established, we can easily predict the properties of a mixed solution from its ratio. The simplest and the most effective method to measure the mixing ratio of the mixed solution is to measure its density. Measuring density does not require expensive equipment and densities can be measured in real time through a Coriolis flow analyzer attached to most chemical process systems.^[4]

A solution is called to be an ideal solution if all substances in a mixed solution have the same molecular size, and there is no interaction between them. The density of the ideal mixed solution changes in linear proportion to the mixing ratio of each component. However, since all substances have different molecular size and there are interactions between them in real mixed solution, the density of the actual mixed solution changes in a nonlinear fashion with respect to the mixing ratio of each component. In general, when each substance in a mixed solution has different molecular sizes (e.g., gravel and sand) or when attractive forces are acting between them, the actual volume of the mixed solution is less than the volume obtained by simply adding up the volumes of each solution. And this volume contraction occurring in the mixed solutions leads to an increase in the density of the mixed solutions. Since it is difficult to analytically estimate the exact size of the molecules contained in the mixed solution, and their interaction, the amount of volume contraction in a mixed solution is predicted mostly by an empirical law. Recently, a relatively simple but quite accurate model for predicting the volume contraction in a mixed solution has been reported, in which the volume contraction in glycerol water mixture is described as the sine function.^[11] The predicted densities of glycerol water mixture at different temperatures have showed the values which was very close to the density experimentally measured. In this study, we investigate the applicability of the model introduced for predicting the density of glycerol water mixture to three dihydric alcohols (ethylene glycol, propylene glycol, 1,3-propanediol) and three monohydric alcohol (methanol, ethanol, and 1-propanol) water mixture. The extension and limitation of the model for glycerol water mixture will be discussed in practical point of view.

2. Theory and Experiment

2.1. Calculation of Density

In this paper, the model proposed by Andreas Volk et al. was used to theoretically calculate the density of an alcohol water mixture. The process for deriving the final formula for calculating the density of an alcohol water mixture is described below. If an alcohol water mixture is an ideal solution, the density of the mixed solution ($\rho_{m,ideal}$) at a specific temperature (T) is determined by the density of an alcohol (ρ_a), the density of water (ρ_w), and the volume of an alcohol and water (V_a, V_w) (Eq. (1)).

$$\rho_{m,ideal}(T) = \frac{\rho_a(T)V_a(T) + \rho_w(T)V_w(T)}{V_a(T) + V_w(T)} \quad (1)$$

In Eq. (1), both terms (density and volume) are dependent on temperature. If the volume is expressed in terms of density and weight, Eq. (1) can be expressed as density (temperature-dependent) and weight (temperature-independent) as in Eq. (2).

$$\rho_{m,ideal}(T) = \frac{\rho_a(T)V_a(T) + \rho_w(T)V_w(T)}{V_a(T) + V_w(T)} \quad (2)$$

Equation (1) is valid only if the mixture is an ideal solution, in which alcohol and water in a mixed solution have the same molecular size, and they do not interact with each other. In this ideal case, the final volume of the mixed solution ($V_{m,ideal}$) is given by simply adding the volume of each solution (Eq. (3)).

$$V_{m,ideal}(T) = V_a(T) + V_w(T) \quad (3)$$

However, in reality, the molecular size of the two substances is different, and there is an interaction between them. Thus, the actual volume of the mixed solution ($V_{m,actual}$) is generally smaller than $V_{m,ideal}$, and its actual density ($\rho_{m,actual}$) is larger than $\rho_{m,ideal}$ estimated from Eq. (1) or (2). Therefore, in order to predict $\rho_{m,actual}$, a correction term (κ) related to volume contraction is required (Eq. (4)).

$$\rho_{m,ideal}(T) = \kappa \cdot \rho_{m,ideal}(T) = \kappa \cdot \frac{\rho_a(T)\rho_a(T)(w_a + w_w)}{w_a\rho_w(T) + w_w\rho_a(T)} \quad (4)$$

The difference between $\rho_{m,ideal}(T)$ and $\rho_{m,actual}(T)$ is resulted from the difference between $V_{m,ideal}(T)$ and $V_{m,actual}$. Therefore, it would be reasonable to define the

volume contraction term (κ) as the ratio between $V_{m,ideal}$ and $V_{m,actual}$ as shown in Eq. (5).

$$\kappa(T) = \frac{V_{m,ideal}(T)}{V_{m,actual}(T)} = \frac{V_a(T) + V_w(T)}{V_{m,actual}(T)} = \frac{\frac{w_a}{\rho_a(T)} + \frac{w_w}{\rho_w(T)}}{\frac{(w_a + w_w)}{\rho_{m,actual}(T)}} \tag{5}$$

$$= \frac{\rho_{m,actual}(T)(w_a \rho_w(T) + w_w \rho_a(T))}{\rho_a(T) \rho_w(T) (w_a + w_w)}$$

As expressed in Eq. (5), the volume contraction term, $\kappa(T)$ is a function of temperature and which is dependent on the weight (w_a, w_w) and density (ρ_a, ρ_w) of alcohol and water, and the actual density of the mixture ($\rho_{m,actual}$). The actual densities of the mixture ($\rho_{m,actual}$) at specific mole fractions, and temperatures are taken from the literature, and fitted using the following Eq. (6) as introduced in Reference 11.

$$\kappa(T) = 1 + A(T)[\sin(w_a^x \cdot \pi)]^y \tag{6}$$

The coefficients x and y were obtained according to the type of mixed alcohol using the least squares method. The volume contraction term, $\kappa(T)$ is expressed as the function of temperature. The optimum value of A dependent on temperature was obtained using the same method (the least squares method) in fixed coefficients of x and y . The prefactor “ A ” was obtained at several specific temperatures, and plotted as the function of temperatures. The trend of A dependent on temperatures was simulated using quadratic equation (Eq. (7)).

$$A(T) = B_2 \cdot T^2 + B_1 \cdot T + IC \tag{7}$$

2.2. Measurement of Density

In order to compare the theoretically obtained density using Eq. (4) with the experimentally measured density, a mixed solution was prepared using various alcohols (glycerol, ethylene glycol, 1,3-propanediol, propylene glycol, methanol, ethanol, and 1-propanol) and water in three specific volume ratio (1:4, 1:1, and 4:1), and their densities were measured using a pycnometer at ambient conditions (1 atm, 21°C). Glycerol (≥99.5%, Aldrich), ethylene glycol (EG, 99.8%, Aldrich), 1,3-propanediol (13-PD, 99.0%, DAEJUNG), propylene glycol (PG, 99.0%, DAEJUNG), methanol (MeOH, 99.5%, DAEJUNG), ethanol (EtOH, 99.9%, DAEJUNG), and 1-propanol (≥99.5%, Aldrich) was used as purchased, and

mixed with deionized water (18.2 MΩ × cm) produced by water purification system (QPAK1; MILLI Pore). Environmental conditions such as humidity and temperature were measured using Humidity-Dew-Point-Wet-Bulb-Traceable Thermometer (4410CC; Traceable). Since density is dependent on environmental condition such as humidity and temperature, Density measurements are conducted three times per sample and averaged with standard deviation.

3. Results and Discussion

Before we extend the applicability of the model proposed by Andreas Volk et al. [11] to other alcohol water mixture, it must be verified that our calculations are performed correctly. In order to confirm this, the calculation results performed in Reference 11 were reproduced.

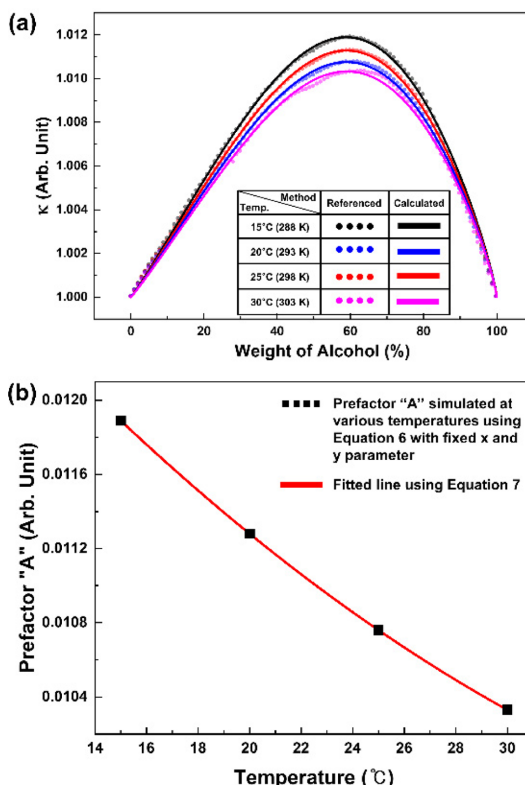


Fig. 1. (a) Correction term (κ) plotted as the function of weight ratio of glycerol, and (b) prefactor, A simulated at various temperature using Eq. (6) [black dots in (b)] in glycerol-water mixtures. The prefactor, A can be fitted by quadratic function of Eq. (7) [red solid line in (b)].

Table 1. Parameters of Eq. (6) for Glycerol water mixtures at various temperatures

Temp.	Parameter	A	x	y
15°C		0.01189	1.30414	0.81551
20°C		0.01128	1.30809	0.81081
25°C		0.01076	1.31067	0.80739
30°C		0.01033	1.31437	0.80731
Ave. \pm S.D.		0.01107 \pm 0.000673325	1.30932 \pm 0.00431	0.81026 \pm 0.00386

The volume contraction term, $\kappa(T)$, of glycerol water mixture was obtained as the function of weight percentage of alcohols at 15, 20, 25, and 30°C. using densities measured in a previous paper [12] and represented by black, blue, red, and pink dotted circles in Fig. 1(a), respectively. As reported, the maximum value of $\kappa(T)$ appears when the weight percentage is about 60%, and the overall value of $\kappa(T)$ gradually decreases as the temperature increases. These results obtained from experimentally measured densities can be simulated using Eq. (6), and three parameters A , x , and y can be obtained at each temperature by the least squares method as represented in Table 1. The values of x , and y parameters do not change significantly with temperature, and their relative standard deviations are ~ 0.3 and $\sim 0.5\%$, respectively. On the other hand, the relative standard deviation of the parameter, A was $\sim 6\%$, which means that the parameter, A quite sensitively depends on the temperature. In order to obtain a general formula adaptable at any temperature, the parameter, A should be expressed as a function of temperature at fixed values of x and y parameters. This may be the reason for obtaining parameter A using fixed parameters 1.31 and 0.81 in Reference 11. Following the same logic, after taking the average values of 1.31 and 0.81 as fixed x and y parameters, the parameter A according to the temperature can be obtained again using the least squares method [black squares in Fig. 1(b)]. By fitting these values with a quadratic function of Eq. (7), red solid line in Fig. 1(b) was obtained, and 1.80×10^{-6} , -1.85×10^{-4} , and 1.43×10^{-2} were obtained as the values of coefficients B_2 , B_1 , and IC , and these values are closed to the literature values, 1.78×10^{-6} , -1.82×10^{-4} , and 1.41×10^{-2} , respectively. Taking into these results, it can be confirmed that our calculation process is correct and the results are well reproducible. We applied the same calculation process to other alcohol water mixtures.

As explained in the introduction part, the model proposed by Andreas Volk et al. was developed to predict the density of only glycerol water mixture. Thus, this model may be well adapted for molecules that are structurally similar to glycerol, but may be difficult to apply to other alcohols as the size or number of hydroxyl groups of alcohols is much different from those of glycerol. In order to ensure our expectation, 6 different mixed solutions containing three dihydric alcohols with different chemical structures (e.g., EG, 13-PD, and PG), and three monohydric alcohols with different number of methyl groups (e.g., MeOH, EtOH, and 1-Propanol) were explored. The volume contraction term, $\kappa(T)$ of each mixture was obtained as the function of weight percentage of alcohols from the densities at 25°C that were referenced from several literatures^[8,12-14] (grey dotted circles in Fig. 2), and simulated by the least square method using Eq. (6) with variable parameters A , x , and y (black solid line in Fig. 2). The simulated results are well matched with experimental data in dihydric alcohol water mixtures [Fig. 2(a-c)], and MeOH water mixture [Fig. 2(d)], however, some deviations between experimentally obtained $\kappa(T)$ and theoretically simulated one appeared in EtOH water mixtures [Fig. 2(e)] and 1-Propanol water mixtures [Fig. 2(f)]. The degree of deviation increases as the number of methyl groups increases from MeOH [Fig. 2(d)] to EtOH [Fig. 2(e)], and finally to 1-Propanol [Fig. 2(f)]. This must be resulted from an increase in hydrophobicity of the alcohols with the number of methyl groups. Although the number of methyl groups of 13-PD and PG is the same as that of 1-Propanol, the reason that the experimentally obtained $\kappa(T)$ is well described by Eq. (6) is probably due to the hydrophilicity by multiple hydroxyl groups. This tendency is consistent with our expectations, but one interesting point is that the model used for glycerol still works well for MeOH, which is much smaller in size

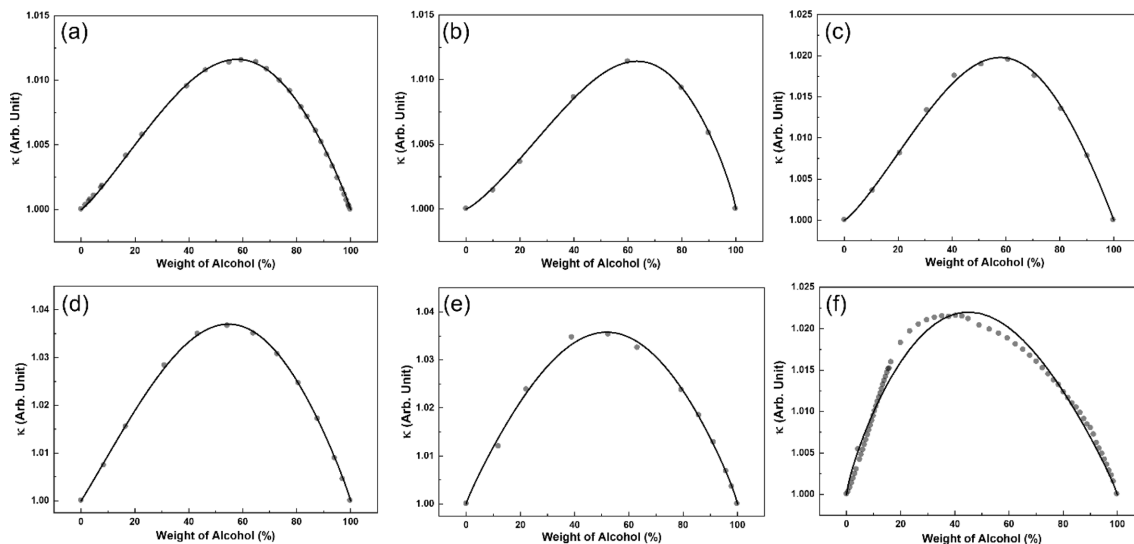


Fig. 2. Correction term κ of (a) ethylene glycol, (b) 1,3-propanediol, (c) propylene glycol, (d) methanol, (e) ethanol, and (f) 1-propanol obtained by Eq. (5) with referenced densities (filled circles), and simulated by Eq. (6) (solid lines) at 298K.

compared to that of glycerol. These results imply that the application of the model proposed by Andreas Volk et al. is determined by the hydrophilicity or hydrophobicity of the molecules rather than their size. In order to obtain a general formula for each alcohol water mixture, the same procedure used for glycerol was repeated, and the parameter A of each alcohol water mixture was obtained at several temperatures with fixed x , and y parameters, and plotted against temperature (Fig. 3). The mixtures containing alcohols with multiple hydroxyl groups (e.g., EG, 13-PD, and PG) show similar tendency with that of glycerol, in which the prefactor, A follows a positive parabolic function [Fig. 3(a-c)], whereas other mixtures containing monohydric alcohols (e.g., MeOH, EtOH, and 1-Propanol) is described as a negative parabolic function [Fig. 3(d-f)]. This can be clearly confirmed by comparing their quadratic coefficient, B_2 [Fig. 4(a)], which is positive for tri- or dihydric alcohols [red squares in Fig. 4(a)] but negative for monohydric alcohols [blue squares in Fig. 4(a)]. Although additional investigations should be required for more alcohols with different structure, based on the results so far, it can be concluded that the tendency of the prefactor A with respect to temperature depends on the number of hydroxyl groups in the alcohol.

Contrary to this tendency, when the values of the

prefactor A for all alcohol water mixtures are compared, it is revealed that they are classified in different way other than the number of hydroxyl groups. As shown in Fig. 4(b), the prefactor A for all alcohol water mixtures are broadly classified into three categories (upper for MeOH and EtOH, middle for 1-Propanol and PG, and lower for Glycerol, EG, and 13-PD). The prefactor A of mixtures containing alcohols with multiple hydroxyl groups Glycerol, EG, and 13-PD) appear in the category with the smallest prefactor A . Interestingly, PG with two hydroxyl groups does not appear in the same category with Glycerol, EG, and 13-PD, but with 1-Propanol in the middle category. It is believed that different category of PG with 13-PD is attributed to their different chemical structure. In the structure of 1-Propanol, two hydroxyl groups are attached to the first and third carbons, and these two hydroxyl groups can effectively cover the second methyl groups, which cannot function as methyl groups exhibiting hydrophobicity. Thus, the chemical structure of 13-PD is different from that of EG, but its chemical properties can be similar to that of EG, resulting in the same category of the prefactor A . On the other hand, although PG has the identical molecular formula with 13-PD, its chemical properties can be different with that of 13-PD, but similar to that of PG, because the methyl group located at the end of the structure can efficiently exhibit hydrophobic properties by

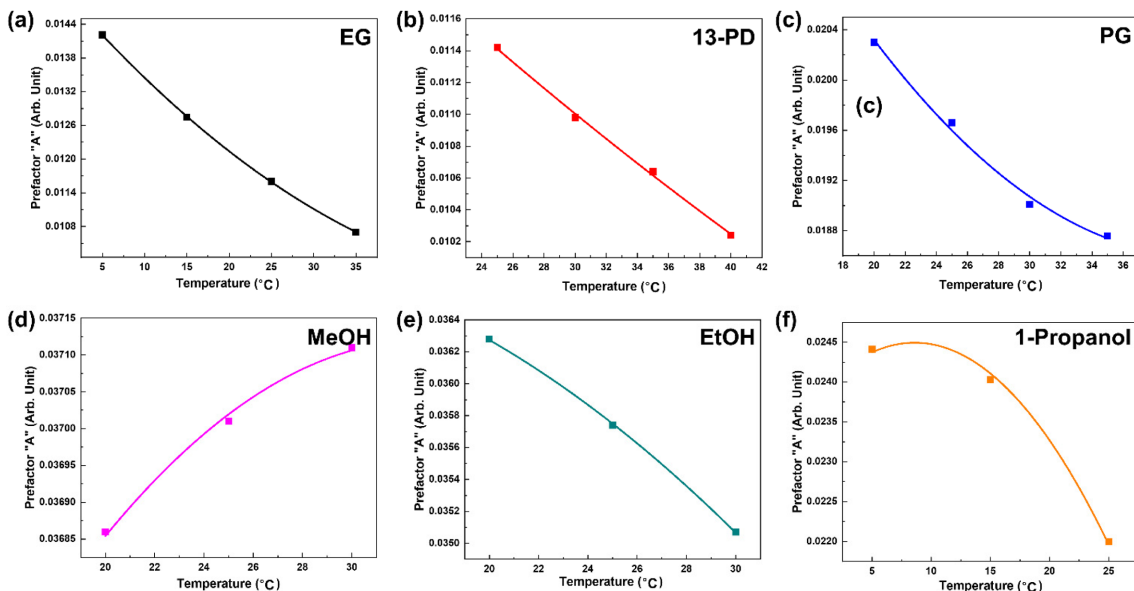


Fig. 3. Prefactor "A" obtained for (a) ethylene glycol, (b) 1,3-propanediol, (c) polyene glycol, (d) methanol, (e) ethanol, and (f) 1-propanol using Eq. (6) (filled circles) and fitted lines using Eq. (7) (solid lines).

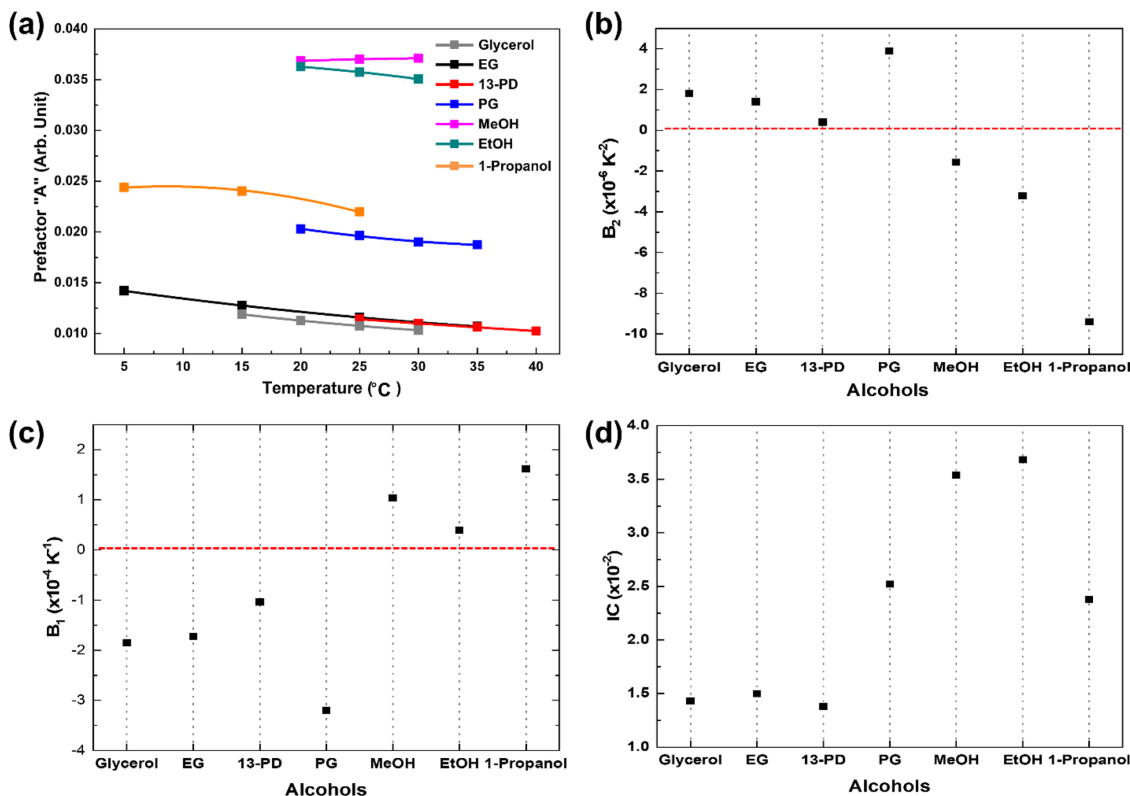


Fig. 4. Comparison of (a) prefactor, A represented as the function of temperature and (b, c, and d) parameter B_2 , B_1 , and IC , respectively for 7 different alcohols

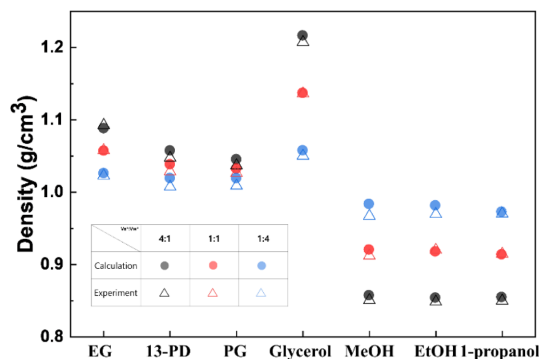


Fig. 5. The calculated densities (filled circles) for 7 different alcohol water mixtures containing ethylene glycol (EG), 1,3-Propanediol (13-PD), propylene glycol (PG), glycerol, methanol (MeOH), ethanol (EtOH), and 1-Propanol were compared to experimentally measured densities (empty triangles) in three specific alcohol water volume ratios (4:1 (80%), 1:1 (50%) and (1:4) 20%).

less hindrance effect of hydroxyl groups. The monohydric alcohols with two or less methyl groups such as MeOH and EtOH also appear in the same upper category. In summary, it is presumed that as the number of hydroxyl groups increases, a lower prefactor A value is exhibited, and a smaller number of methyl groups tends to exhibit a higher prefactor A value.

To prove the accuracy of the model developed for calculating alcohol-water mixtures density, various alcohols (Glycerol, EG, 13-PD, PG, MeOH, EtOH, and 1-Propanol) were mixed with water in three different volume ratios (1:4, 1:1, and 4:1), and their densities were measured by the pycnometer at ambient conditions (1 atm, 21°C), and compared to calculated ones (Fig. 5). To quantify the deviation between calculated density and experimentally measured density, the error range is defined as the ratio between the deviation of two values and experimentally measured density $|\rho_{cal} - \rho_{exp}|/\rho_{exp}$, where ρ_{cal} and ρ_{exp} represent the calculated, and measured density, respectively. The error range obtained at each volume ratio was averaged, and their averaged error range of each alcohol water mixture was 0.49% for glycerol, 0.26% for EG, 0.94% for 13-PD, 0.77% for PG, 1.1% for MeOH, 0.67% for EtOH, and 0.28% for 1-Propanol. Overall, the calculated densities (filled circles in Fig. 5) are well matched with experimental values (empty triangles in Fig. 5) as represented their small averaged small error range. Interestingly,

based on the results of Fig. 2, the calculated density of 1-Propanol and the experimental values were expected to show a large deviation, but its deviation was not very large.

3. Conclusion

In this paper, we extended the density model developed for predicting the density of only glycerol water mixture to other alcohol water mixture systems. The applicability of the model was investigated for various mixtures containing 6 different alcohols (e.g., EG, 13-PD, PG, MeOH, EtOH, and 1-Propanol). The simulation parameters are mainly dependent on the number of hydroxyl groups, rather than the molecular sizes, but more different alcohols should be tested. Overall, the calculated densities are consistent with the measured values within small error range of 0.64%, which means that the model proposed by Andreas Volk et al. is well applicable to other alcohol (at least, EG, 13-PD, PG, MeOH, EtOH, and 1-Propanol) water mixtures.

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