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The Viscosity of Glycerol−Water Mixtures Including the Supercooled Region

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ABSTRACT: The dynamic viscosity of water, glycerol, and its mixtures over a wide range of temperatures, including the supercooled region, was calculated resorting to several predictive approaches and compared to published data. The temperature dependence of the viscosity of the pure components can be described within the experimental error using different empirical equations. However, the best fit is obtained by the Avramov−Milchev equation, taking into account that this equation has only two adjustable parameters. The same model was also used to describe the viscosity of the mixtures over the entire range of temperatures and compositions where experimental data are available and to extrapolate the viscosities of the mixtures at temperatures close to the glass transition. We calculated the viscosities of glycerol−water mixtures, over the entire range of compositions, between (238.15 and 273.15) K. The agreement with experimental data in the stable liquid region is very good, which makes our predictions in the supercooled region fairly reliable. The analysis of the glycerol−water mixtures reveals that, in contrast to that previously found in other aqueous polyol solutions such as sucrose and trehalose, the temperature and composition dependence of the viscosity cannot be described with a scaled Arrhenius equation. At low temperatures, the excess viscosity of the glycerol−water mixtures can be very well described by a regular-like solution coefficient.

1. INTRODUCTION

For more than 50 years the now classical book *The properties of gases and liquids* by Reid, Prausnitz, and Sherwood[1] (authored by Poling, Prausnitz, and O'Connell in the fifth edition published in 2001) has been a reference material for chemical engineers searching for methods to estimate the thermodynamics and transport properties of pure and multicomponent mixtures of gases and liquids.

In the chapter devoted to viscosity, Prausnitz and coauthors discussed the temperature and pressure dependence of the viscosity of pure liquids emphasizing that, while the viscosity of water at room temperature increases only a little over 2-fold from room pressure up to 10^3 MPa, the viscosity of glycerol (and many other liquids) increases more than 2 orders of magnitude on the same pressure range. Regarding the temperature dependence, they noted that a modified Andrade's equation,[2] a widely used correlation for the effect of temperature (T) on the viscosity (η) of liquids, having the form,

$$\eta = A \exp\left(\frac{B}{T + C}\right) \tag{1}$$

where A, B, and C are constants, fails at low temperatures, "as liquids sometimes show a sharp increase in viscosity as the freezing point is approached". Thus, proposed empirical prediction methods (all of them group-contribution methods) can be used to calculate the viscosities of pure liquids with reasonable confidence from temperatures (20, 30) K above the freezing point.[1]

This important observation anticipated what, later, Angell[3] described as the behavior of fragile liquids, that is, liquids that exhibit a "super-Arrhenius" temperature dependence of the viscosity or the structural relaxation time. The fragility, m, of a liquid is measured by the viscosity deviation from the Arrhenius behavior at the glass transition temperature, T_g, and is defined by,

$$m = \left[\frac{\partial \log_{10} \eta}{\partial (T_g/T)}\right]_{T_g} \tag{2}$$

Actually, eq 1 has the form of the Vogel−Tammann−Fulcher (VTF) equation,[4] which describes quite reasonably the viscosity temperature dependence of fragile liquids,

$$\eta = \eta^0 \exp\left(\frac{DT_0}{T - T_0}\right) \tag{3}$$

where η^0, D, and T_0 are constants. The parameter D decreases with increasing curvature of the Arrhenius plot and is inversely related to the fragility.

Glycerol is a typical glass former with a glass transition temperature of $T_g \approx 193$ K and a moderated fragility.[5] Water, on the other hand, crystallizes very easily below the nucleation temperature, unless cooling is performed at very high rates. Thus, the first determinations of the glass transition temperature of water were performed by extrapolating the glass

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transition temperature of glycerol—water mixtures to zero polyol concentration.[6,7]

Glycerol aqueous solutions are resistant to crystallization and, at high polyol concentrations, are excellent glass formers which are commonly used as a cryoprotector media.[8,9] It is precisely their cryoprotectant role that makes the properties of glycerol—water mixtures at low temperature of practical interest.

The aim of this work is to develop a representation of the concentration and temperature dependence of the viscosity of glycerol—water mixtures for estimating this property in the supercooled regime, as close as possible to the glass transition temperature. We compare our results with a previous description of the viscosity of aqueous glycerol in the supercooled regime,[9] where only the pure components viscosity data were used as fitting parameters. In our opinion, that approach is not reliable considering that it could lead to viscosity extrapolated values far from the experimental ones. Finally we will propose a representation of the viscosity of glycerol—water mixtures that improves the estimations in the supercooled regime.

2. DATA SOURCES

2.1. Pure Water. The viscosity of water is well-known in the stable and supercooled region. The IAPWS recommended a correlation equation for the viscosity of water from 253.15 K and the pressure of the triple point up to 1173 K and 300 MPa,[10,11] including subzero viscosity data from different sources with variable accuracy.[12−16] Osipov et al.[16] determined the viscosity of metastable water down to 239.15 K, the lowest temperature reached in supercooled water, but the uncertainty of these data (3 %) are larger than those reported at higher temperatures. Thus, for metastable supercooled water, the proposed correlation is in fair agreement (within 5 %) with available data down to 253.15 K.[10,11]

Pátek et al.[17] proposed a simpler equation valid between (253.15 and 383.15) K at 0.1 MPa,

$$\eta(\mu\text{Pa}\cdot\text{s}) = \sum_{i=1}^{4} a_i T_r^{\,b_i} \qquad (4)$$

where $T_r = T/300$ K, with the corresponding coefficients, a_i and b_i, summarized in Table 1. Equation 4 predicts the viscosity of supercooled water down to 253.15 K within 5 %, while the agreement is 1 % over the entire stable region.

2.2. Pure Glycerol. Several authors have studied the viscosity of pure glycerol using different experimental techniques. Tammann and Hesse[18] pioneered the study of the viscosity of supercooled fluids including glycerol and reported measurements from (268.95 down to 231.15) K. Old measurements, at temperatures between (293.15 and 303.15) K, were summarized by Sheely,[19] while Parks and Gilkey[20] determined the viscosity of supercooled glycerol between (221.15 and 186.15) K, that is, in the supercooled and glassy state, using a Coutte cell. However, the reliability of the data close to the glass transition is uncertain.

Piccirelli and Litowitz[21] determined the viscosity of glycerol between (267.15 and 313.15) K, using a Hoeppler viscosimeter, and used ultrasonic probe techniques to determine the shear modulus down to 231.15 K. Huck et al.[22] measured the viscosity of glycerol at temperatures down to 186.15 K using a penetroviscometer. Schöter and Donth[23] used a parallel plate rheometer to determine the viscosity of glycerol from (213 to 323) K.

Table 1. Parameters for the Calculation of the Viscosity of Water at Various Temperatures with eq 4

	a_i	b_i	a_i	b_i
i	$253.15 < T/\text{K} < 383.15$		$239.15 < T/\text{K} < 383.15$	
1	280.68	−1.9	749.95	−4.6
2	511.45	−7.7	53.39	−13.2
3	61.13	−19.6	55.70	−22.0
4	$45.90 \cdot 10^{-2}$	−40.0	$5.77 \cdot 10^{-4}$	−71.7

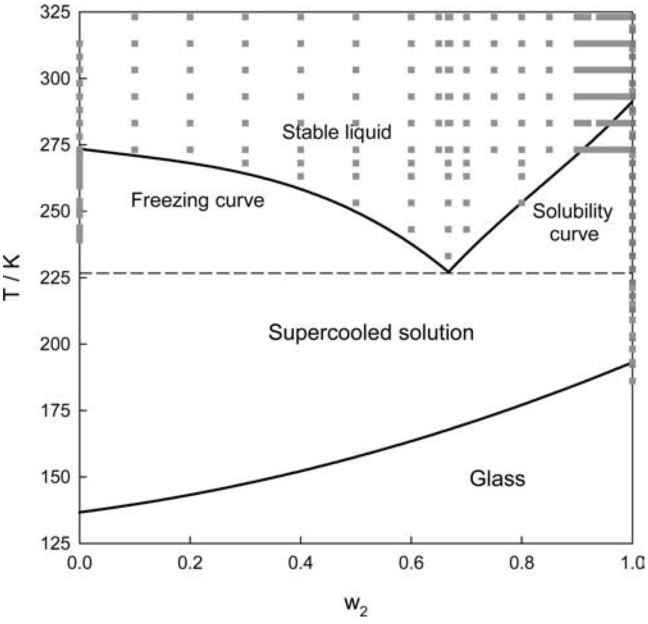

Figure 1. Supplemented phase diagram of the glycerol—water system showing the equilibrium freezing temperature of water, the solubility curve of glycerol, and the glass transition curve. The gray points indicate the region of the phase diagram where viscosity data are available in the literature.[12−16,18−23,26]

Klyachenko and Litvinov[24] performed viscosity measurements on glycerol between (243.15 and 323.15) K using a capillary viscosimeter, while a "microscopic" viscosity in the same range of temperature was measured by photon correlation spectroscopy using latex particles 34 nm in diameter. They reported, in the supercooled region, an increase of the microscopic viscosity as compared to the macroscopic one, which was assigned to structural heterogeneities in the fluid. However, this anomaly was discarded by Dixon and Nagel,[25] who repeated the experiments using polystyrene spheres with radii between (10 and 102) nm and found no differences between the microscopic and macroscopic viscosities over the entire temperature range.

2.3. Glycerol—Water Mixtures. Segur and Oberstar[26] reported the viscosity of aqueous glycerol solutions from (273.15 to 373.15) K over the entire range of compositions. The study, performed with Cannon and Feske viscometers, aimed to correct some inaccuracies found in previous data and provided a comprehensive comparison with older results on narrower temperature and composition ranges.

According to the supplemented phase diagram of the glycerol—water system[27] shown in Figure 1, the above-mentioned data cover only a very small region in the supercooled regime, for glycerol mass fractions, w_2, higher than 0.92.

Shankar and Kumar[28] measured the kinematic viscosity of glycerol—water mixtures all over the range of composition in the interval of temperatures between (283.15 and 323.15) K, using Ubbelohde viscometers. More recently, Chenlo et al.[29] measured the kinematic viscosity of aqueous solutions containing glycerol and sodium chloride. For the glycerol—water binary mixtures the measurements between (293.15 and 323.15) K cover the water-rich region ($w_2 < 0.32$).

Guzmán et al.[30] measured the viscosity of glycerol—water mixtures at 308.15 K to probe that viscosity can be determined quantitatively by optical trapping interferometry. Their results were presented only in graphical form.

Viscosities of glycerol—water solutions below $T = 273.15$ K were reported by Dow[31] without mentioning the way in which the data were obtained.

3. THEORETICAL BACKGROUND

It is well-known that the temperature dependence of the viscosity of supercooled simple organic liquids cannot be described over the entire range of temperature with a single equation,[32] like VTF or the equivalent Williams, Landel, and Ferry (WLF) equation,[33] which in its linear version can be expressed as,

$$\frac{(T - T_g)}{\ln(\eta/\eta_g)} = \frac{C_2}{C_1} - \frac{(T - T_g)}{C_1} \tag{5}$$

η_g being the viscosity at the glass transition temperature, and C_1 and C_2 are constants. This is also the case for pure glycerol over the temperature range from (193.15 to 323.15) K, as shown previously.[23,34]

Stickel et al.[35] observed that the temperature derivative of the VFT eq 3,

$$\left(-\frac{\partial \ln \eta}{\partial T}\right)^{-1/2} = \frac{T - T_0}{(DT_0)^{1/2}} \tag{6}$$

can be used to determine the viscosity temperature dependence change, that is, the crossover temperature. Therefore, VFT equations can be used to describe the temperature dependence of the viscosity in the supercooled and stable liquid regimes using different coefficients (η^0, D, and T^0) above and below the crossover or Stickel temperature.

The use of VFT-like equations can be avoided by resorting to empirical viscosity-temperature correlations having more than three adjustable parameters, as that proposed by Chen and Pearlstein[36] for the viscosity of glycerol,

$$\eta = \eta^0 \exp\left(\frac{A}{T^3} + BT + \frac{C}{T}\right) \tag{7}$$

where $\eta^0 = 1.00758 \cdot 10^{-8}$ Pa·s, $A = 2.21895 \cdot 10^8$ K^3, $B = 7.99323 \cdot 10^{-3}$ K^{-1}, and $C = 880.469$ K. This equation fits the viscosity between (273.15 and 373.15) K with an average error of 1.07 %, slightly better than the five-parameter equation proposed by Stengel et al.[37] for the kinematic viscosity. The limited range of temperature employed in this analysis prevented the authors to find a change of regime, besides the use of multiple fitting parameters would probably hide out the anomaly.

The viscosity representation of glycerol—water mixtures is challenging because of its composition dependence. Even when the strong-fragile nature of supercooled water is a matter of controversy,[38,39] it is accepted that concentrated aqueous solutions of glycerol behave as fragile fluids.

A simple approach, already analyzed by Chen and Pearlstein,[36] is to use eq 7 describing the viscosity T-dependence with parameters η^0, A, B, and C that depend on composition.

Shankar and Kumar[28] described the temperature and composition dependence of the kinematic viscosity, ν, of glycerol—water mixtures through the following expression,

$$\frac{\ln \nu - \ln \nu_1}{\ln \nu_2 - \ln \nu_1} = x_2[1 + x_1(a + bx_2 + cx_2^{\,2})] \tag{8}$$

where x_2 is the glycerol mole fraction, ν_1 and ν_2 are the kinematic viscosities of pure water and glycerol, respectively, at the same temperature of the mixture, and the parameters a, b, and c are temperature-dependent.

The predictive value of these approaches is very limited because the T- or c-dependent parameters were fitted over a narrow range of temperatures or compositions.

A similar problem was addressed recently by Longinotti and Corti in the study of the viscosity of sucrose and trehalose aqueous solutions which, as glycerol, are also used in cryoprotection.[40] Both disaccharide aqueous solutions can be described with reasonable accuracy by using an scaled Arrhenius representation in terms of the reduced temperature $T^* = T_g/T$,

$$\ln \eta = a + bT^* + cT^{*2} + dT^{*3} \tag{9}$$

where a, b, c, and d are constants. The physics behind this formulation is simple: the viscosity of the mixtures at a given temperature depends only on the difference with the glass transition temperature, that is, the composition dependence is implicit in the variation of T_g with composition.

Other empirical equations were used to describe the viscosity of sucrose and trehalose aqueous solutions, the most successful being the four parameters Génotelle equation,[41]

$$\ln \eta = a + bx_2 + \Phi(c + dx_2^{\,n}) \tag{10}$$

where a, b, c, d, and n are constants and $\Phi = (30 - t)/(91 + t)$ is a function of the temperature t (in Celsius).

A similar approach, combining temperature and composition dependence in the correlation, was proposed by Chenlo et al.[29] for the kinematic viscosity of dilute aqueous glycerol solutions over a small interval of temperature between (293.15 and 323.15) K,

$$\frac{\nu}{\nu_1} = 1 + am \exp\left(\frac{m^b}{cT_R^{\,3} + d}\right) \tag{11}$$

where m is the glycerol molality, $T_R = T/273.15$ K, and a, b, c, and d are fitting parameters.

Cheng[42] developed a similar correlation that includes the temperature and concentration dependence,

$$\nu = \nu_1^{\,\alpha} \nu_2^{\,(1-\alpha)} \tag{12}$$

where α is a parameter which depends on the mass fraction of glycerol, w_2, and the temperature

$$\alpha = 1 - w_2 + \frac{a(T)b(T)(1 - w_2)w_2}{aw_2 + b(1 - w_2)} \tag{13}$$

with $a = 0.705 - 0.0017T$, and $b = (4.9 + 0.036T)a^{2.5}$. This correlation was used to fit the data by Segur and Oberstar,[26] Shankar and Kumar,[28] and Chenlo et al.[29] with average errors of 1.3 %, 2.3 %, and 0.7 %, respectively.

He et al.[9] have calculated the viscosity of glycerol, sucrose, trehalose, and fructose aqueous solutions, over the entire range of compositions and at temperatures down to 140.15 K using the WLF (eq 5). The viscosity of the mixtures at the glass transition temperature was calculated assuming that it depends on the molar volume of the mixture, but values at room temperature were used to calculate viscosities near or below the glass transition temperature. The calculated viscosity values of water around 140.15 K differ by several orders of magnitude for the four systems studied. However, the value for glycerol−water mixtures is close to 10^{11} Pa·s.

For estimating the viscosity of pure water these authors employed the free volume model,[43,44] which can be expressed as,

$$\eta = \eta^0 \exp\left[\frac{V^*}{A(B - T_g + T)}\right] \tag{14}$$

where $\eta^0 = 3.33 \cdot 10^{-5}$ Pa·s, $A = 5.93 \cdot 10^{-4}$ cm^3·g^{-1}·K^{-1}, and B = 30.12 K are parameters of the model, fitted between (273.15 and 333.15) K. $V^* = 0.91$ cm^3·g^{-1} is the specific volume of the liquid water at 0 K, and T_g = 136 K.

Avramov and coworkers[45,46] developed a model which determines the temperature dependence of the average jump frequency of molecules and, through it, the viscosity temperature dependence,

$$\eta = \eta^0 \exp\left(\frac{A}{T}\right)^{\alpha} \tag{15}$$

where η^0, A, and α are fitting parameters. This three-parameter correlation was modified to include the glass transition temperature as an adjustable parameter, defining T_g as the temperature where the viscosity equals $\eta_g = 10^{12.5}$ Pa·s,

$$\eta = \eta^0 \exp\left[(28.75 - \ln \eta^0)\left(\frac{T_g}{T}\right)^{\alpha}\right] \tag{16}$$

where the viscosity is measured in Pa·s. Avramov[46] fitted the viscosity of glycerol using eq 16 with $\eta^0 = 6.3 \cdot 10^{-4}$ Pa·s, T_g = 177 K, and α = 3.2.

Recently, Mauro et al.[47] derived a model for the viscosity of glass-forming liquids based on the Adam−Gibbs equation[48] which relates the viscosity to the configurational entropy of the liquid.

The temperature dependence of the viscosity in this model is given by,

$$\eta = \eta^0 \exp\left[\frac{A}{T} \exp \frac{B}{T}\right] \tag{17}$$

where η^0, A, and B are fitting parameters. The authors expressed eq 17 in terms of T_g, defined as the temperature where $\eta_g = 10^{12}$ Pa·s,

$$\eta = \eta^0 \exp\left\{(27.6 - \ln \eta^0)\frac{T_g}{T} \exp\left[\left(\frac{m}{(27.6 - \ln \eta^0)} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]\right\} \tag{18}$$

where m is the fragility defined by eq 2. The authors discussed this model in comparison with the VFT and the Avramov−Milchev equations and concluded that eqs 17 and 18 offer a realistic extrapolation of the configurational entropy in the high- and low-temperature limits.

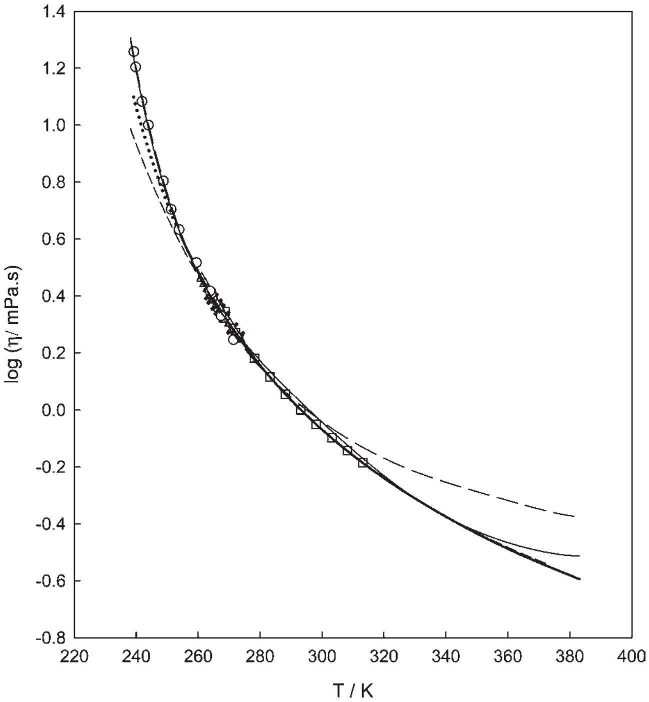

Figure 2. Viscosity of pure water as a function of temperature. Experimental data: △, ref 12; □, ref 13; ×, ref 15; ○, ref 16; thick —, the IAPWS recommended values vs T between (253.15 and 383.15) K, ref 17; · · ·, the extrapolated values down to T = 239.15 K; - - -, the fit to eq 14; thin —, the fits to eq 4, at T between (239.15 and 383.15) K.

4. RESULTS AND DISCUSSION

In this section we analyze the temperature dependence of the viscosity of the pure liquids on their corresponding metastable intervals and the viscosity of the glycerol−water mixtures in the region between (273.15 down to 239.15) K, where viscosity data for both components are available.

As shown in Figure 1, the viscosities of pure water[12−16] and pure glycerol[18−23] have been reported on very different temperature ranges in the corresponding supercooled region. In the case of water the available data extend close to the homogeneous nucleation temperature (235 K), which is far from the glass transition temperature of water (136 K). On the other hand, the stability of glycerol upon cooling extends to temperatures close to the glass transition temperature (195.4 K), that is, the data for supercooled glycerol cover a wider range of temperature as compared to water.

4.1. Viscosity of the Pure Components.

Figure 2 shows the viscosity of water at 0.1 MPa from (239.15 to 383.15) K.[12−17] It is clear that the extrapolation of eq 4 beyond the validity region, with parameters given by Pátek et al.,[17] yields values around 100 % lower than the experimental ones at the lowest temperature (close to the homogeneous nucleation temperature, T_h = 235 K). Even worse is the performance of eq 14, which departures from the experimental data at temperatures lower than 263.15 K.

We have refitted the experimental data using eqs 4 and 14 including the subzero data. The agreement with the experimental data is excellent in the low temperature region for both models, but the fits deteriorate in the high temperature region, particularly

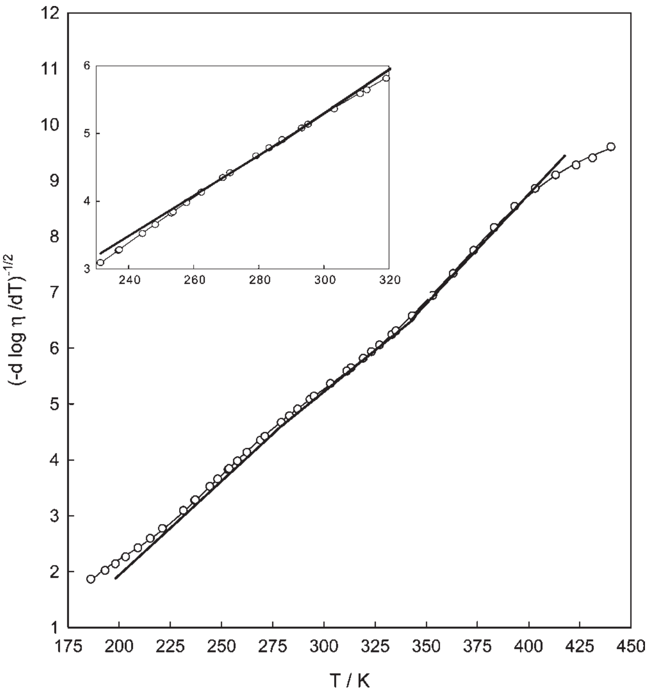

Figure 3. Stickel plot for glycerol using all of the data sources[18−22] except that by Schöter and Donth.[23] —, the fit reported in ref 23. The inset shows a magnification of the crossover region.

in the case of the free volume model, where the difference between the experimental and calculated viscosity is more than 50 % at 373.15 K, compared with an average 3 % for eq 4.

In summary, the correlation proposed by Pátek et al.[17] seems to describe with reasonable accuracy the viscosity of liquid and supercooled water at 0.1 MPa. The coefficients of eq 4 over the extended range of temperature are given in Table 1.

The viscosity of glycerol has been analyzed in detail in the supercooled region. The Stickel temperature[35] was found to be close to 283 K by Schröter and Donth[23] using eq 6. This crossover temperature is consistent with that obtained from dielectric measurements.[23] On the other hand, Magazú and Migliardo[34] found a change of regime at 234.65 K, but the source of data used by these authors is uncertain and this crossover temperature was obtained by analyzing the slope of the Arrhenius plot, which is not a well established procedure as that proposed by Stickel et al.[35]

We have used the Stickel derivative (eq 6) to determine the validity of the VFT equation for glycerol over a wider temperature range. For this purpose we used all the available data except those from Schröter and Donth.[23] The results, shown in Figure 3, seem to indicate two changes of regime located around (343 and 263) K. The inset in Figure 3 shows in detail the region close to the crossover temperature reported by Schröter and Donth,[23] where it is clear that the change of slope for the data of these authors is opposite to that found for all of the rest of data sources. Even when the difference is small, our guess is that the accuracy of the viscosity measurements performed by Schröter and Donth is higher than the older results.

A third crossover temperature is also observed in Figure 3 at ∼393 K. Considering that the only source of data above 373.15 K is that reported by Dow[31] without mentioning the origin and accuracy of the data, we conclude that the viscosity of glycerol on this temperature range should be considered with caution.

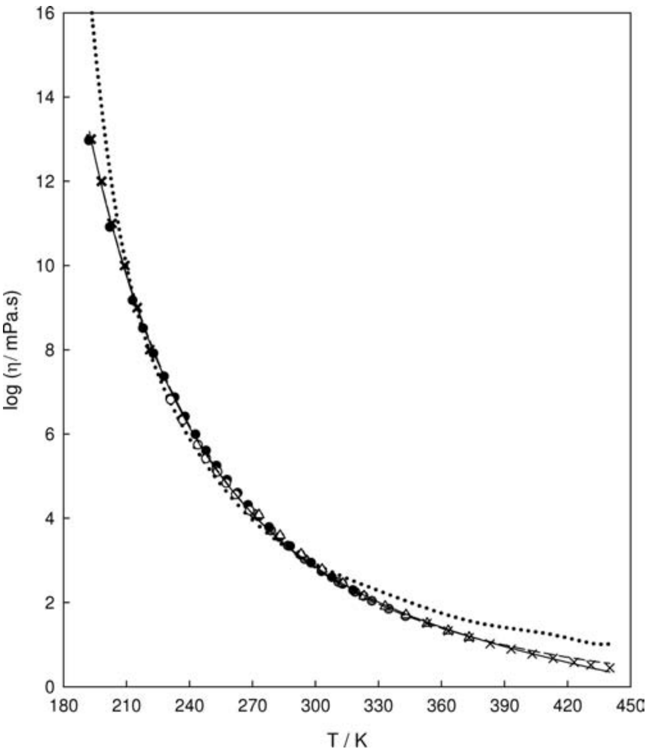

Figure 4. Experimental viscosity of pure glycerol as a function of temperature: **X**, ref 20; ●, ref 23; ×, ref 31; gray ●, ref 21; △, ref 26; ○, ref 18; —, fit to eq 7; · · ·, fit to eq 5, ref 9; - - -, fit to eq 16.

To fit the viscosity of glycerol from 373.15 K down to the glass transition temperature we tested VFT-like equations like eqs 5 and 16 or semiempirical equations such as eq 7. The experimental and calculated viscosities are shown in Figure 4.

It can be observed that the WLF equation with the parameters used by He et al.[9] overestimates the viscosities in both the high- and the low-temperature regions (dotted line in Figure 4). It is surprising that these authors used the WLF correlation to predict the viscosities of pure glycerol and its aqueous solutions at temperatures down to 140.15 K, in the glycerol glassy state, even when this correlation overestimates the viscosity by several orders of magnitude in the supercooled region close to the glass transition, as can be seen in Figure 4.

The four-parameter eq 7 was refitted to the experimental data from (193.15 to 433.15) K, and the estimated viscosities are in excellent agreement with the experimental ones (solid line in Figure 4) when the following parameters are used: $\ln(\eta^0/\text{mPa}\cdot\text{s}) = 25.8709$, $A = 3.0942\cdot 10^8\ \text{K}^3$, $B = -0.0327\ \text{K}^{-1}$, and $C = -6291.03$ K.

Finally, the viscosity of pure glycerol was fitted with eq 16 over the entire temperature range with a very good agreement, except for the higher temperature tail ($T > 403.15$ K) where differences up to 50 % are found. It should be remarked that eq 16 was used with only two adjustable parameters: $\ln(\eta^0/\text{mPa}\cdot\text{s}) = -0.8086$ and $\alpha = 3.2729$. The glass transition temperature of glycerol was fixed at the experimental value, $T_g = 195.4$ K, and the viscosity at the glass transition was $10^{12.5}$ mPa·s. As mentioned in Section 3, Avramov fitted the glycerol viscosity data using η^0, α, and T_g as adjustable parameters and fixing the viscosity at T_g as $\eta_g = 10^{12.5}$ Pa·s. The best fit yields $T_g = 177$ K, which is a value almost 20 K lower than the experimental one. Since the choice $\eta_g = 10^{12.5}$ Pa·s is arbitrary, we prefer to fix T_g at the experimental value, and

Table 2. Avramov–Milchev Parameters (eq 16) and Glass Transition Temperature (T_g) of Glycerol–Water Mixtures, Estimated with eqs 19 and 20, for the Calculation of the Viscosity as a Function of the Glycerol Mass Fraction, w_2

w_2	T_g/K	$\ln(\eta^0/\text{mPa}\cdot\text{s})$	α
1.0	195.4 ± 0.2[a]	−0.809 ± 0.110[b]	3.273 ± 0.026[b]
0.9	186.0 ± 0.1	−1.082 ± 0.026	3.361 ± 0.009
0.8	177.9 ± 0.2	−0.955 ± 0.070	3.554 ± 0.026
0.7	171.0 ± 0.2	−0.890 ± 0.051	3.732 ± 0.021
0.6	165.1 ± 0.1	−0.923 ± 0.087	3.863 ± 0.043
0.5	160.0 ± 0.1	−1.183 ± 0.047	3.843 ± 0.025
0.4	155.4 ± 0.1	−1.432 ± 0.038	3.799 ± 0.022
0.3	151.4 ± 0.2	−1.535 ± 0.027	3.824 ± 0.017
0.2	147.7 ± 0.3	−1.669 ± 0.018	3.822 ± 0.012
0.1	144.3 ± 0.4	−1.843 ± 0.024	3.777 ± 0.016
0.0	141.0 ± 0.8	−2.194 ± 0.147	3.623 ± 0.074

[a] Deviation calculated as $|T_g^{\text{exp.}} - T_g^{\text{calc.}}|$. [b] Standard deviation of the nonlinear least-squares fit

η_g at 195.4 K was interpolated from the experimental data from Parks and Gilkey[20] and Schoter and Donth,[23] as $\eta_g = 10^{12.5}$ mPa·s. We will come back to the discussion of this choice of η_g in the next section, in relation with the estimation of the viscosities of glycerol–water mixtures.

Nevertheless, it should be noted here that the value of the viscosity of glycerol at the glass transition is more than 2 orders of magnitude lower than that reported at 186.15 K,[20] which corresponds to glassy glycerol, according with the more recent data on the glass transition of glycerol.[49–53] The expected value of viscosity at T_g is 10^{12} Pa·s for a glass-forming liquid, but the slope of the viscosity versus temperature curve is very large near the glass transition point, so the viscosity could change by a factor between 100 and 1000 within a few degrees Celsius in that region.

4.2. Viscosity of the Water–Glycerol Mixtures. To test the scaled Arrenhius equation, eq 9, for the viscosity of aqueous glycerol solutions as a function of w_2, we fitted the glass transition temperature of these solutions as a function of concentration to the available experimental data,[6,7,49–54] using the polynomial expression:

$$T_g(\text{K}) = 140.3 + 35.272w_2 - 3.879{w_2}^2 + 23.467{w_2}^3 \quad (19)$$

The glass transition temperature for pure glycerol ($w_2 = 1$) is 195.2 K. We also fitted the experimental data with the equation given by Gordon and Taylor:

$$T_g = \frac{w_2 T_{g2} + k_{GT}(1 - w_2)T_{g1}}{w_2 + k_{GT}(1 - w_2)} \quad (20)$$

were T_{g2} is the glass transition temperature of pure glycerol, T_{g1} the glass transition temperature of pure water, and k_{GT} the Gordon–Taylor constant. The obtained results are T_{g2} = (195.5 ± 0.5) K, T_{g1} = (141.8 ± 1.1) K, and k_{GT} = 1.95 ± 0.12. The standard deviation of the fit is 1.4 K, quite similar to that obtained with eq 19. It should be noticed that the values predicted for T_{g1} for both equations differ significantly from the commonly accepted value, T_{g1} = 136 K. This could be explained considering that the measurement of the glass transition temperature of rich water glycerol aqueous solutions has higher errors in comparison to glycerol-rich mixtures, due to the big tendency of water to crystallize. T_g values for aqueous glycerol given by the Gordon and Taylor eq 20 and the polynomial eq 19 agree within the standard deviation of the fits. Therefore, in Table 2 we report the mean value of both fits, also used to draw the supplemented phase diagram shown in Figure 1 and data in Figure 5.

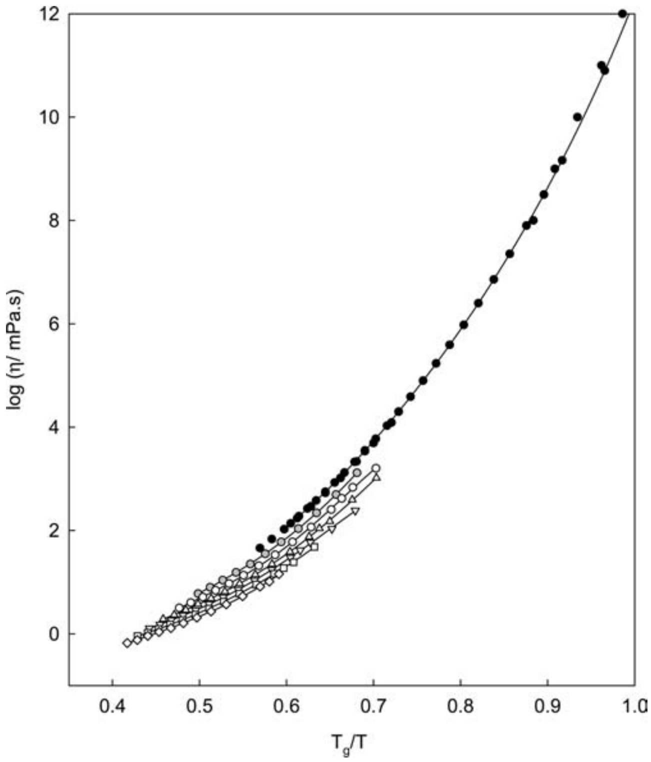

Figure 5. Arrhenius representation of the viscosity, where T is scaled to T_g, for glycerol and glycerol–water mixtures. Glycerol mass fraction w_2: ●, 1.0, refs 20, 21, and 23; gray ●, 0.9, ref 26; ○, 0.8, ref 26; △, 0.7, ref 26; ▽, 0.6, ref 26; □, 0.5, ref 26; ◇, 0.4, ref 26.

Figure 5 shows that the scaled Arrhenius curves corresponding to different glycerol contents do not merge on a common curve, as found for trehalose and sucrose aqueous solutions.[40] Indeed, at a given T_g/T value, the difference between the viscosity of pure glycerol and that of a mixture containing 40 % (w/w) of glycerol (w_2 = 0.4) is close to 1 order of magnitude. It should be emphasized that this observation is independent of which equation is used to fit the glass transition temperature of the solution and which set of experimental T_g data are used in the fit.

The Génotelle eq 10 was also tested to fit the viscosity of these mixtures, considering the coefficients of the reduced temperature, Φ, as adjustable parameters. The best fit was obtained with coefficients: a = 6.568, b = 15.837, c = 8.713, and d = 16.781, with $\Phi = -(102.82 + t)/(142.51 + t)$, and n = 1.091. In spite of having seven fitting parameters, the deviations in the predictions of viscosity are typically around 10 %, reaching values close to 40 % for certain compositions and temperatures, mainly below 273.15 K and for the pure components.

Figure 6 depicts the viscosity of the mixtures for compositions in the range $0.4 < w_2 < 1$, along with the predictions by He et al.[9] using the WLF equation with the viscosity at the glass transition calculated by the following expression:

$$\eta_g = {\eta_g}^0 \exp[k(x_1 V_1 + x_2 V_2)] \quad (21)$$

where ${\eta_g}^0 = 1.44\cdot 10^{11}$ Pa·s and $k = 0.074$ mol·cm^{-3} are parameters of the model, while $V_1 = 18$ cm^3·mol^{-1} and

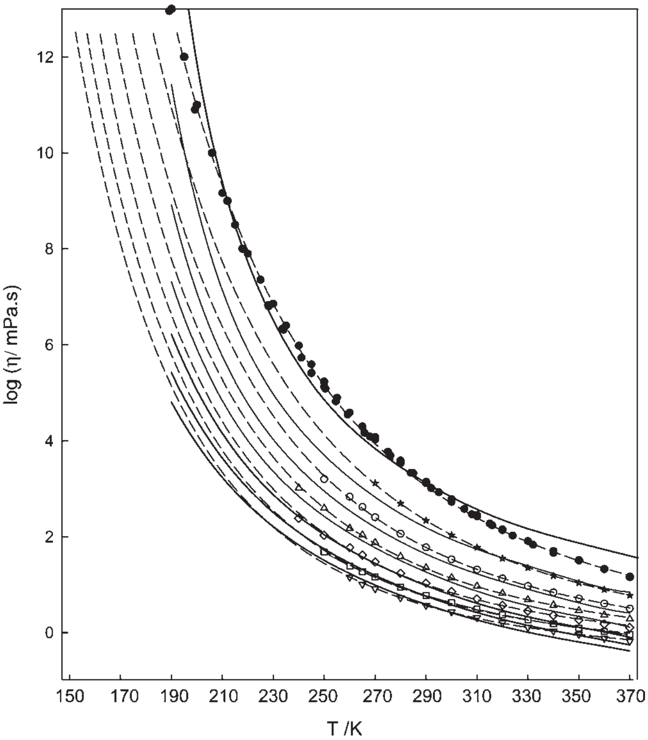

Figure 6. Logarithm of experimental viscosity of glycerol−water mixtures versus absolute temperature for w_2: ●, 1.0, refs 20, 21, and 23; ☆, 0.9, ref 26; ○, 0.8, ref 26; △, 0.7, ref 26; ◇, 0.6, ref 26; □, 0.5, ref 26; ▽, 0.4, ref 26; —, predictions with the WLF eq 20, with parameters given in ref 9; - - -, predictions with the eq 16.

V_2 = 73.3 $\text{cm}^3\cdot\text{mol}^{-1}$ are the molar volumes of pure water and glycerol, respectively, at 298.15 K. That is, η_g is calculated from the ideal volume of the mixture at 298.15 K, which is supposed to be constant over the entire range of temperature. Probably this crude assumption is responsible for the strong deviations of the calculated viscosities to the experimental values, a fact already discussed in relation to the temperature behavior of the viscosity of pure glycerol. Thus, the WLF equation underestimates the viscosity of glycerol-rich solutions ($w_2 > 0.7$) in the temperature region ($313.15 > T/\text{K} > 238.15$), and also for water-rich solutions ($w_2 < 0.7$) above 313.15 K.

Considering these results, and taking into account the excellent performance of the Avramov−Milchev eq 16 in the case of pure glycerol, we decided to use this equation for fitting the experimental viscosity data of glycerol aqueous solutions in the entire range of compositions, $0 \leq w_2 \leq 1$, including the pure components.

The results are shown in Figure 6, where the predictions extend to viscosities of $10^{12.5}$ mPa·s, that is, the value adopted for the viscosity of all of the mixtures and pure liquids at the glass transition temperature. Thus, only two adjustable parameters are used for fitting the viscosities at each composition, and they are shown in Table 2. The fact that an unique choice of η_g allows a good fit of the viscosity of all of the mixtures, even the water-rich ones, indicates that the use of the Avramov−Milchev eq 16 as a two-parameter equation is reasonable.

It should be noted that, as shown in Figure 7, the composition dependence of these parameters is rather simple and can be expressed by:

$$\ln(\eta^0/\text{mPa}\cdot\text{s}) = 2.1686 - 2.7096w_2 + 1.4449{w_2}^2 \qquad (22)$$

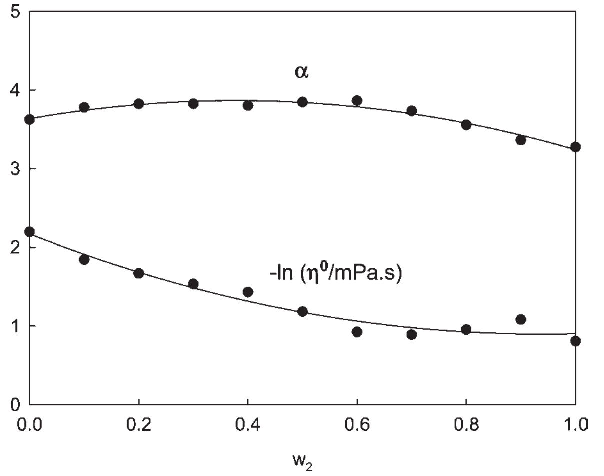

Figure 7. Parameters of the fit with eq 16 as a function of glycerol mass fraction.

$$\alpha = 3.6344 + 1.2198w_2 - 1.6142{w_2}^2 \qquad (23)$$

The agreement with the experimental results is excellent, being the standard deviation within (2 to 5) %. Figure 8 shows the results of the fitting in the region of temperature $220 < T/\text{K} < 373$, covering the subzero region down to the eutectic temperature, and including water-rich mixtures and pure water. It can be observed that the agreement is also excellent for the water-rich solutions, but it deteriorates for pure water below 253.15 K, where the only experimental data are those by Osipov et al.[16] having the greatest uncertainty.

The estimated viscosities for glycerol−water mixtures are summarized in Table 3 for temperatures between (273.15 and 238.15) K, covering the supercooled regions located to both sides of the eutectic point. The agreement with the experimental data, in the region where they are available,[26,31] is better than 10 % with the exception of the value for pure glycerol at 273.15 K where the differences are close to 30 %. This singularity is due to the high experimental dispersion observed for the viscosity of glycerol close to that temperature, as observed in Figure 6.

The vertical solid line in Figure 8 indicates the limit temperature, 239.15 K, where viscosity data are available for the pure components,[12−16,18−23] and the viscosity of the mixtures could be calculated by resorting to mixture rules, as those expressed by eqs 8 and 12. However, these correlations are expressed in terms of the kinematic viscosities and require the knowledge of the densities of the solutions. We will not test this type of representations, but instead, we will analyze the behavior of the excess viscosity, η^{ex}, defined as,

$$\log \eta = [(1 - x_2)\log \eta_1 + x_2 \log \eta_2] + \log \eta^{\text{ex}} \qquad (24)$$

where η_1 and η_2 are the viscosities of water and glycerol, respectively, and x_2 is the mole fraction of glycerol. The term in brackets represents the ideal viscosity of the mixture.

One of the simplest correlations for liquid mixture viscosity data is the one-parameter equation by Grunberg and Nissan,[55] which is recommended for binary systems, except for aqueous solutions.[56,57]

We determined the ideal viscosity of the glycerol−water mixtures in the range of temperatures ($238.15 < T < 373.15$) K, using the best fit of the experimental pure glycerol and water viscosity data using eq 16. The smoothed values of the experimental viscosities of the mixtures,[26,31] shown in Figure 6 and Table 3, were used to calculate the excess viscosity from eq 24. The results for log η^{ex} are shown in Figure 9 as a function of glycerol mole fraction at different temperatures.

It can be observed that the glycerol—water system presents positive excess viscosity over the entire range of composition and temperature. The magnitude of the nonideality is important and increases with decreasing temperature. The symmetry of the curve seems to increase as temperature decreases, and the maximum is located close to $x_2 = 0.5$ at temperatures lower than 313.15 K. Although the curves at low temperatures are not perfectly symmetric, the use of a regular solution coefficient of the form,

$$\log \eta^{ex} = (1 - x_2)x_2 G_{12} \qquad (25)$$

to express the composition dependence of log η^{ex}, G_{12} being the glycerol—water interaction coefficient, seems reasonable for viscosity predictions at temperatures below 238.15 K. If this is the case, the behavior of the glycerol—water supercooled mixtures would be simpler than that observed at moderated and high temperatures.

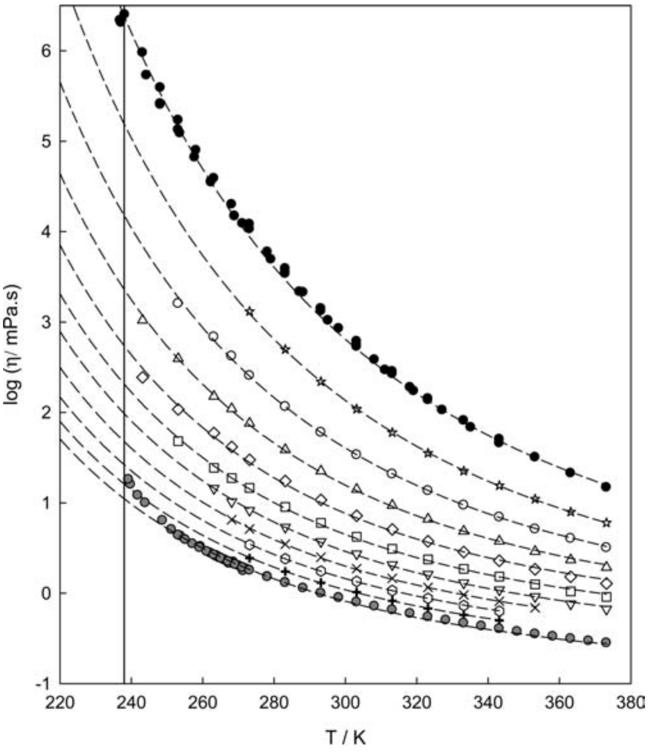

Figure 8. Logarithm of experimental and predicted viscosity by eq 16 for glycerol—water mixtures versus absolute temperature for w_2: ●, 1.0, refs 21, 23, 26, and 31; ☆, 0.9, ref 26; ○, 0.8, refs 26, 31; △, 0.7, refs 26, 31; ◇, 0.6, refs 26, 31; □, 0.5, refs 26, 31; ▽, 0.4, refs 26, 31; ×, 0.3, refs 26, 31; ⬡, 0.2, ref 26; +, 0.1, ref 26; gray ●, 0.0, refs 12 to 16; - - -, the fit with eq 16.

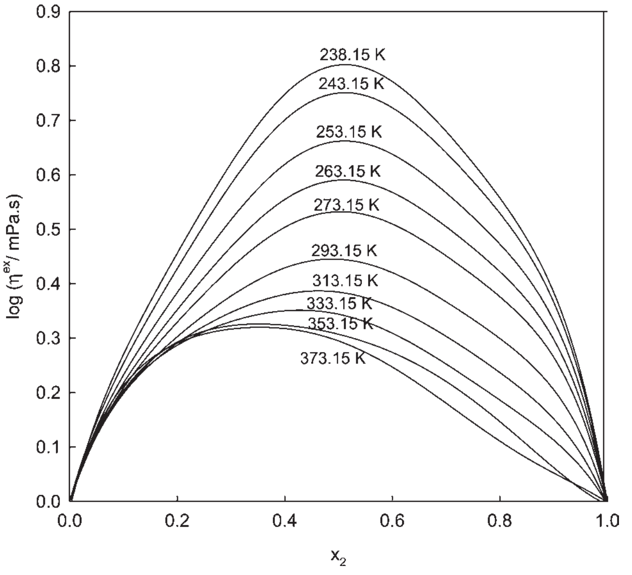

Figure 9. Excess viscosity of the glycerol—water mixtures as a function of the glycerol mole fraction at different temperatures.

Table 3. Experimental and Calculated (eq 16) Viscosities of Glycerol—Water Mixtures (in mPa·s) as a Function of Glycerol Mass Fraction (w_2) at Temperatures between (238.15 and 273.15) K

T/K		w_2 = 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
273.15	exp.[26]	2.44	3.44	5.14	8.25	14.6	29.9	76	255	1310	12070
	calc.	2.48	3.49	5.23	8.41	14.2	27.8	72	252	1243	8758
268.15	exp.[31]	----	----	6.5	10.3	18.8	41.6	110	419	----	----
	calc.	3.02	4.32	6.6	10.9	18.8	38.0	104	391	2103	16220
263.15	exp.[31]	----	----	----	14.4	24.4	58.1	151	683	----	----
	calc.	3.75	5.46	8.5	14.5	25.5	53.6	156	631	3721	31610
258.15	exp.	----	----	----	----	----	----	----	----	----	----
	calc.	4.76	7.05	11.3	19.7	36.0	78.2	242	1063	6914	65190
253.15	exp.[31]	----	----	----	----	48.1	108	394	1600	----	----
	calc.	6.18	9.34	15.4	27.7	52.2	118	392	1880	13570	$1.431 \cdot 10^5$
248.15	exp.	----	----	----	----	----	----	----	----	----	----
	calc.	8.23	12.7	21.5	40.3	78.6	187	666	3507	28300	$3.366 \cdot 10^5$
243.15	exp.[31]	----	----	----	----	----	244	1046	----	----	----
	calc.	11.3	17.9	31.3	60.9	123	309	1194	6946	63135	$8.552 \cdot 10^5$
238.15	exp.	----	----	----	----	----	----	----	----	----	----
	calc.	16.0	26.1	47.2	96.0	203	540	2272	14712	$1.519 \cdot 10^5$	$2.367 \cdot 10^6$

Obviously, the measurement of viscosities of glycerol−water solutions in the deep supercooled region ($T < 238.15$ K) should be encouraged to probe this hypothesis.

5. CONCLUSIONS

We have developed a predictive approach to calculate the dynamic viscosity for water, glycerol, and its mixtures on a wide temperature range, which includes the supercooled region of water (up to 239.15 K) and glycerol (up to 193.15 K).

It has been shown that the viscosity of the pure components can be described within the experimental error using different empirical equations, although the Avramov−Milchev[45] eq 16, having only two adjustable parameters described quite well for the temperature dependence of their viscosities. Moreover, the analysis of the data of the pure components using this VFT-like equation allowed us to be cautious about the reliability of some sources of data, particularly those reported for glycerol above 373.15 K and for water below 253.15 K.

The analysis of the glycerol−water mixtures reveals that, in contrast to that previously found in other aqueous solutions of cryoprotectans polyols (sucrose and trehalose), the temperature and composition dependence of the viscosity cannot be described by a scaled Arrhenius equation.

The good performance of eq 16 to describe the viscosity of the mixtures over the entire range of temperature and compositions where experimental data are available renders a procedure to extrapolate the mixture viscosities at temperatures close to the glass transition. On the basis of this fact we could calculate the viscosities of the glycerol−water mixtures, over the entire range of compositions, from (273.15 down to 238.15) K. The agreement with experimental data in the stable liquid region is very good, what makes our predictions in the supercooled region fairly reliable.

Finally, the smoothed experimental data were employed to calculate the excess viscosity of the mixtures over the entire range of temperature were the viscosity of the pure components is available. The results indicate that at low temperatures the glycerol−water mixtures seem to behave as regular solutions, that is, the excess viscosity can be described with a single interaction parameter.

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DEDICATION

Dedicated to Prof. John Prausnitz, for his long and fruitful contribution to experiments, theory, and education in the field of molecular thermodynamics.

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