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Glycerol Aqueous Solutions

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ABSTRACT.

The diffusion of ferrocene methanol in supercooled glycerol-water mixtures has been measured over a wide viscosity range, which allowed analyzing the composition dependence of the Stokes-Einstein breakdown (diffusion-viscosity decoupling). The observed decoupling exhibits a common behavior for all studied compositions (glycerol mass fractions between 0.7 and 0.9), determined by the reduced temperature (T/T_g) of the mixtures. This result differs from that reported previously for the diffusion of glycerol in its aqueous solutions, where the reduced temperature for the decoupling decreases with increasing water content. We conclude that the contradictory results are only apparent, and they can be explained by the use of inconsistent extrapolated values of the viscosity of the glycerol-water mixtures in the supercooled region.

KEYWORDS. Water, polyols, Stokes-Einstein rrelation, breakdown, ferrocene methanol.

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1. INTRODUCTION

The behavior of deeply supercooled and glassy materials is, since more than two decades, one of the most exciting issues in the physics of condensed matter.[1,2] A drastic viscous slow down occurs when a liquid is supercooled and approaches the glass transition temperature, which among other important phenomena, leads to the breakdown of the classical hydrodynamic theory expressed by the Stokes-Einstein (SE) relation:[3]

$$D = \frac{k_B T}{6\pi\eta\, r} \tag{1}$$

which predicts the diffusion coefficient, D, of a spherical probe of radius r in a continuum solvent having bulk viscosity η, with k_B the Boltzmann constant and T the temperature.

The predictions of Eqn. (1) are valid in stable liquids and even in supercooled glass forming systems, well above the glass transition temperature (T_g); but at a critical temperature close to $1.2T_g$ the dynamics become complex and the SE relation fails to describe the viscosity-diffusion relationship.[4-7] The decoupling between D and η, which depends on the size relationship between the diffusing molecule and those of the surrounding media,[8,9] as well as on the type of interactions,[10] has been extensively studied in pure liquids. On the contrary, our knowledge of the properties of supercooled mixtures and their dependence on composition are scarce.[11]

Pure water cannot been supercooled in the temperature interval between the homogenous nucleation temperature (≈ 230 K) and T_g (≈ 136 K), the region called "no-man´s land" by Stanley and coworkers,[12] due to water crystallization. However, aqueous solutions containing hydrogen bonding or ionic solutes, such as sucrose, glycerol or LiCl, can be easily supercooled and the

glass transition temperature can be tuned by adjusting the nature and concentration of the non-aqueous component.

Most of the experimental information on the mobility of solutes in supercooled mixtures corresponds to polyol aqueous solutions, which are commonly used as cryoprotectants. Thus, the diffusion-viscosity decoupling was observed for fluorescein (a fluorescent probe) in sucrose-water mixtures,[13] and also for the intradiffusion coefficients of water in carbohydrate (sucrose and trehalose) aqueous mixtures.[14] We have also studied the diffusion-viscosity decoupling of fluorescein disodium salt in supercooled aqueous sucrose and trehalose solutions,[15] and of ferrocene methanol in sucrose aqueous solutions.[16] The picture emerging from these studies is that the mobility of the bulky solutes is not directly coupled with the water mobility in the disaccharide-water mixture, as is the case for small ionic solutes.[17,18] The SE relationship is obeyed over a restricted region at high values of the reduced temperature (T/T_g), while below a critical T/T_g value, diffusion decouples from viscosity.

Chen et $al.$[19] have analyzed the effect of the mixture composition in the diffusion of glycerol in glycerol-water mixtures using ^{1}H NMR. Their results show that the decoupling reduced temperature for the diffusion coefficient of glycerol decreases with increasing water content in the concentration range between 0.85 and 1.00 glycerol mass fractions, w. The authors claimed that the frustration-limited continuous cluster model proposed by Kivelson and coworkers,[20,21] or the dynamical heterogeneities model by Jung et $al.$[22] could explain this behavior. Thus, they suggested that increasing the water content in the mixture would postpone the formation of domains or dynamical heterogeneities, and would inhibit the breakdown of the SE relation.

On the contrary, our results for the diffusion of the fluorescein disodium probe in supercooled aqueous saccharide solutions[15] seem to indicate that the decoupling reduced temperature does not

depend on the composition of the aqueous mixture, even considering that our data covers a narrow composition range. This is in contradiction with the conclusions reached by Chen *et al.*[19] because the dependence of the decoupling temperature with composition, if real, should also be observed for fluorescein disodium salt, unless the size of the domains is smaller than this probe. In order to get a deeply understanding of the decoupling in binary aqueous solutions, we have measured the diffusion of ferrocene methanol, a probe with a size similar to that of glycerol, in supercooled aqueous glycerol solutions, covering a wide composition range (with glycerol mass fractions w = 0.2, 04, 06, 0.7, 0.8 and 0.9). The aim of this work is to analyze the effect of composition in the diffusion-viscosity decoupling behavior of ferrocene methanol, and compare our results with previous diffusion data of glycerol in its aqueous solutions.

2. EXPERIMENTAL METHODS

2.1 Materials

Aqueous solutions were prepared with glycerol (J.T.Baker), KNO_3 (Merck) as supporting electrolyte, ferrocene methanol (Aldrich, 97%) and water deionized through a Millipore filter. All chemicals were used as received without further purification. The solutions were prepared by dissolving the corresponding amount of ferrocene methanol (1-3 $mmol.dm^{-3}$) and supporting electrolyte (KNO_3, 0.13 $mol.dm^{-3}$) into the water-glycerol solution (w between 0.2 and 0.9) by immersion in an ultrasonic bath for approximately 5 minutes. Glycerol aqueous solutions containing the supporting electrolyte without ferrocene methanol were used to determine the residual current in the chronoamperometric runs.

2.2 Chronoamperometry with microelectrodes

Ferrocene methanol was selected as the electroactive probe because it is soluble in supercooled water-glycerol solutions and shows a simple one-electron reversible electro-oxidation on Pt, as indicated in Figure 1.
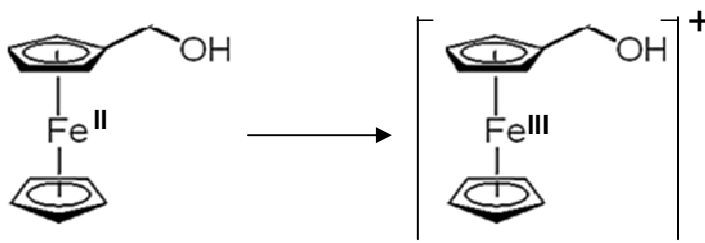
Figure 1: Ferrocene methanol structure and oxidation reaction

Thus, ferrocene methanol diffusion coefficients can be determined by resorting to the chronoamperometric response of its oxidation on disk or cylindrical microelectrodes, using the experimental methodology developed by Longinotti and Corti.[16]

For disk microelectrodes the limiting current, i_L, following a potential step is given by:

$$i_L = 4nFc^*Dr \qquad (2)$$

where n is the number of electrons transferred by molecule, F is Faraday´s constant and c^* is the bulk concentration of the electroactive molecule.

For cylindrical microelectrodes of radius r and length l (large enough to neglect boundary effects) the time dependence of the current after a potential step under diffusion control is given by:[23]

$$\frac{i(t)}{nFDc*l} = 2\pi f(\theta) \tag{3}$$

where $\theta = Dt/r^2$, and the complex function $f(\theta)$ can be approximated by the relationship proposed by Szabo,[24]

$$f(\theta) = \frac{e^{-0.1\sqrt{\theta\pi}}}{\sqrt{\theta\pi}} + \frac{1}{\ln\left[\left(4\theta e^{-\gamma}\right)^{1/2} + e^{5/3}\right]} \tag{4}$$

At long times the current varies inversely with $\ln t$, and a quasi-stationary state is achieved.

Cylindrical Pt microelectrodes were used for solutions with higher viscosities because the current collected in the micro-disk was very small under these conditions. The counter-electrode was a Pt foil (3.5 cm^2) and the reference electrode was Ag/AgCl/KCl(aq) at temperatures above the freezing point of the solution, while the aqueous solution was replaced by an ethanol-water solution (50% v/v) below the freezing point.

The effective radii of the Pt microelectrodes were determined at 25 ^{o}C in aqueous solutions containing K$_4$Fe(CN)$_6$ (0.18-0.41 mM) and KNO$_3$ (0.13 M) by steady state voltammetry for the disc microelectrode, and applying a potential step and following the current *vs*. time curve in the interval 0.15 − 8 seconds for the cylindrical microelectrodes. The diffusion coefficient of the

ferrocyanide ion reported by Moorcroft *et al.*[25] (D = 6.88.10^{-6} cm^2.s^{-1}) was used in the calculations.

The mean diameter of the disc microelectrode was close to 25 μm, while for the cylindrical microelectrodes the diameter varied between 46 and 56 μm for the different electrodes used in this work, which had a length close to 25 mm. Two or more wires were connected in parallel in order to obtain appropriate current responses in very viscous mixtures.

The temperature control was performed with a cryostat (Techne TU-16D) with an accuracy of ± 0.05 K.

Diffusion coefficients of ferrocene methanol were measured over an extended range of glycerol mass fractions, w, between 0.20 and 0.90. Measurements in pure glycerol were not possible using this method since glycerol oxidation current on the microelectrode overpassed that of ferrocene methanol oxidation, leading to unacceptable uncertainties.

3. RESULTS AND DISCUSSION

Table 1 summarizes the measured diffusion coefficients of ferrocene methanol in glycerol-water mixtures at various temperatures, along with the glass transition temperatures and viscosities of the solutions. The glass transition temperatures of the glycerol aqueous solutions were evaluated using the Gordon-Taylor equation:

$$T_g = \frac{wT_{gg} + k_{GT}(1-w)T_{gw}}{w + k_{GT}(1-w)} \tag{5}$$

where T_{gg}= 195.4 K is the glass transition temperature of pure glycerol, T_{gw}= 141.8 K the glass transition temperature of pure water, and k_{GT}= 1.95.[26] The standard deviation of the fit over the whole composition range was ± 1.4 K, but the error in the estimation of T_g is even smaller in the glycerol-rich region covered in this work.

The viscosities of the glycerol-water mixtures reported in the literature, along with the recent data determined in the supercooled regime,[26] were fitted as a function of temperature by resorting to the equation derived from the Avramov-Milchev model.[27,28] The standard deviation of the log (η/mPa.s) fit *vs.* composition and temperature was 0.074, as reported previously.[29]

Table 1: Glass transition temperatures, viscosities, and diffusion coefficients of ferrocene methanol in glycerol-water solutions.

w	T_g (K)	η (mPa.s)	*T* (K)	$D(cm^2.s^{-1})$
0.2	147.9	1.522	298.1	$(4.3 \pm 0.2).10^{-6}$
		2.036	288.1	$(2.9 \pm 0.2).10^{-6}$
		2.872	278.1	$(1.83 \pm 0.09).10^{-6}$
		4.323	268.1	$(1.17 \pm 0.04).10^{-6}$
0.40	155.5	3.049	298.1	$(2.5 \pm 0.1).10^{-6}$
		4.337	288.1	$(1.6 \pm 0.2).10^{-6}$
		6.577	278.1	$(9.4 \pm 2.3).10^{-7}$
		10.79	268.0	$(6.8 \pm 1.4).10^{-7}$
		14.11	263.4	$(4.0 \pm 0.2).10^{-7}$
		19.53	258.1	$(2.6 \pm 0.2).10^{-7}$
0.60	165.1	27.92	273.1	$(2.6 \pm 0.5).10^{-7}$

		38.52	268.0	$(1.6 \pm 0.3).10^{-7}$
		54.08	263.1	$(1.2 \pm 0.1).10^{-7}$
		78.06	258.1	$(8.4 \pm 0.8).10^{-8}$
		118.9	253.2	$(4.8 \pm 0.7).10^{-8}$
0.70	171.0	1588	242.7	$(8.7 \pm 0.6).10^{-9}$
		6500	232.6	$(2.2 \pm 0.4).10^{-9}$
0.80	177.9	1164	258.6	$(7.6 \pm 3.3).10^{-9}$
		4249	248.0	$(2.8 \pm 0.9).10^{-9}$
		4642	247.3	$(4.7 \pm 1.2).10^{-9}$
		17813	238.2	$(1.2 \pm 0.4).10^{-9}$
0.90	185.9	15400	253.0	$(4.4 \pm 0.6).10^{-10}$
		70620	243.1	$(3.8 \pm 0.7).10^{-10}$
		154780	238.6	$(2.0 \pm 0.3).10^{-10}$

Figure 2 summarizes the obtained results for the diffusion of ferrocene methanol in the glycerol-water mixtures as a function of the reduced temperature (T/T_g). It can be observed the slowdown of the translational diffusion of the ferrocene methanol probe as the temperature approaches the glass transition. It is interesting to notice that the diffusion coefficients vary monotonously with the reduced temperature, independently of the glycerol-water composition. Errors for log D, not shown in Figure 2, are between 0.015 and 0.19, according to the data reported in the last column of Table 1.
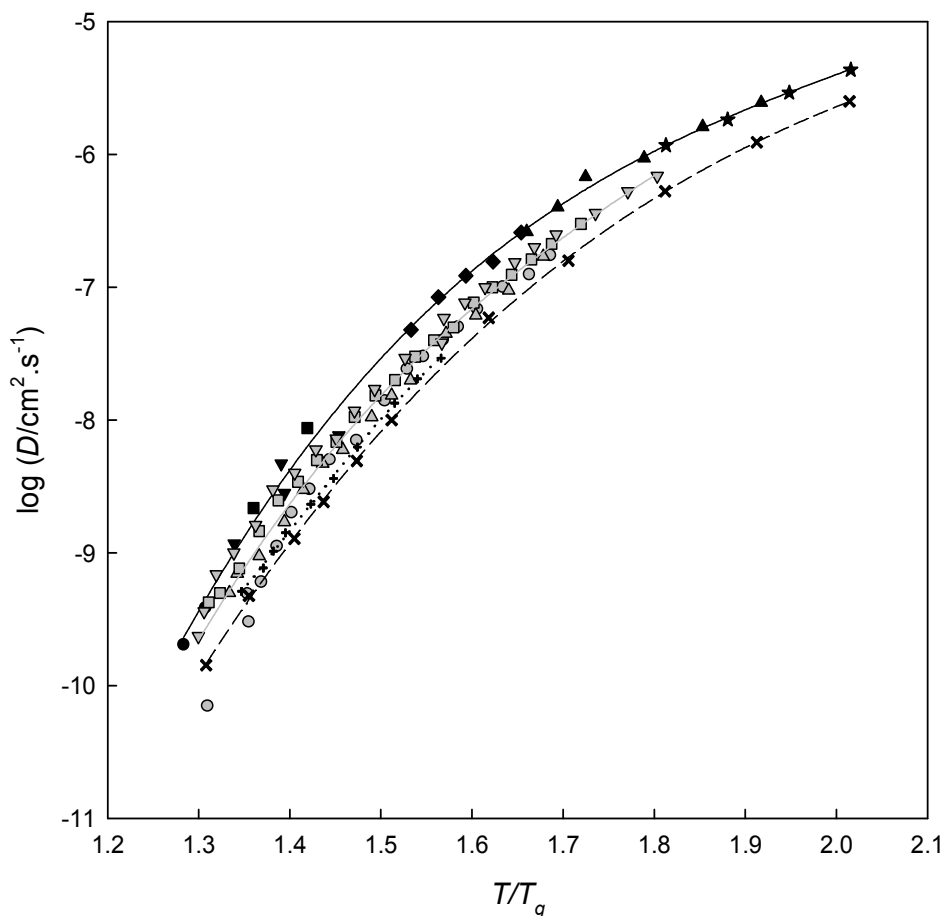
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Figure 2: Diffusion coefficient as a function of the reduced temperature (T/T_g) for: i) ferrocene

methanol in glycerol-water mixtures at w = 0.2 (★); w = 0.4 (▲); w =0.6 (◆); w = 0.7 (■); w =

0.8 (▼); w = 0.9 (●) (solid line corresponds to the best fit); ii) glycerol in glycerol-water

mixtures at w = 0.85 (▼); w = 0.90 (■); w =0.95 (▲); w = 1.00 (●)[19] (gray solid line corresponds

to the best fit of the data, excluding pure glycerol); w = 1.0 (✗)[30] (dashed line corresponds to

best fit); w = 1.0 (✚)[31] (dotted line corresponds to best fit).

Also shown in Figure 2 are the glycerol diffusion coefficients reported by Chen *et al.*[19] for

glycerol mass fractions between 0.85 and 1.00. For comparison we also included in Figure 2

results for the diffusion of pure glycerol measured by Chang and Sillescu,[30] from gradient NMR, and more recently by Kruk *et al.*[31] by means of field cycling NMR relaxometry. Systematic differences are evident when comparing the data by Chen *et al.* and those reported by other authors, particularly in the low temperature range (T/T_g< 1.4), where low self diffusivity of glycerol seems to deviate from the general tendency.

Despite the large scatter in glycerol diffusion data in the low temperature region in the pure solvent, it is clear that a trend similar to that found for ferrocene methanol is observed, that is, the diffusion coefficient scales with T/T_g for all the studied compositions. It should be stressed that T_g for the different water-glycerol mixtures were calculated by resorting to the Gordon-Taylor Eqn. (5) instead of using the empirical formula proposed by Chen *et al.*[19] Differences between both sets of calculations were around 5-6 K for the pure components and up to 10 K for the mixtures, being the T_g values calculated using the Gordon-Taylor equation in better agreement with the more recent literature data for these mixtures (standard deviation ± 1.4 K). Nevertheless, if the T_g values are calculated as reported by Chen *et al.*,[19] only a slight shift in the reduced temperature is observed, without modifying the general pattern observed in Figure 2.

A test of the validity of the SE relation for ferrocene methanol in glycerol-water mixtures is shown in Figure 3, where the ratio $D\eta/T$ is plotted as a function of the reduced temperature. According to the errors estimated for the viscosity, temperature and diffusion coefficient, the error bars plotted for log ($D\eta/T$) are dominated by the errors in log D, while the error bars for T/T_g (< 1.5 K) are smaller than the symbols size.

The decoupling temperature for the diffusion of ferrocene methanol is independent of the mixture composition, in opposition to the results reported by Chen *et al.*[19] for the diffusion of glycerol in its aqueous mixtures. Even though the scatter in the data is relatively high, owing

mainly to the dispersion in the diffusion coefficients, it can be stressed that the decoupling reduced temperature determined for ferrocene methanol in glycerol aqueous solutions, $w = 0.7$, 0.8 and 0.9, does not show a defined trend with composition. Moreover, it can be noticed that the SE product observed below the decoupling reduced temperature can be fitted with a common line for all the analyzed compositions between 0.7 and 0.9 glycerol mass fractions, in opposition to the behavior observed by Chen *et al.*[19] For $T/T_g > 1.5$ the SE relation holds within the experimental error giving a solvation radius close to 0.33 ± 0.06 nm for the slip boundary conditions ($A = 6\pi$ in Eqn. 1), in good agreement with the values obtained, above the decoupling temperature, for the diffusion of ferrocene methanol in sucrose-water mixtures[16] (0.28 nm $< r <$ 0.33 nm) and close to the crystallographic radius of ferrocene (0.27 nm).[32] Thus, it can be concluded that ferrocene methanol behaves essentially as a non-solvated probe in the glycerol-water mixtures.
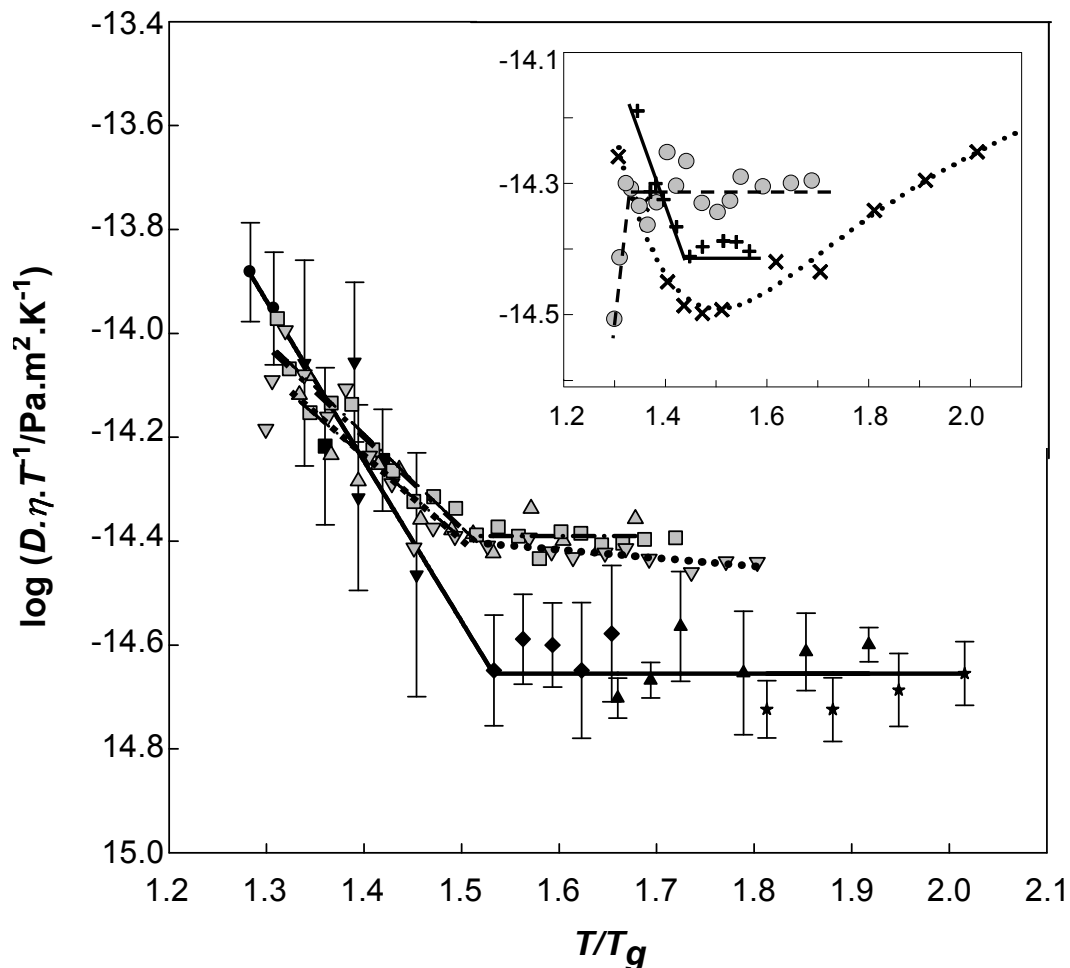
Figure 3: Stokes-Einstein ratio as a function of the reduced temperature for the diffusion of ferrocene methanol and glycerol in glycerol-water mixtures (symbols as in Figure 2). The solid line corresponds to the fit of the experimental data of ferrocene methanol, the dashed line to the diffusion of glycerol data for $w = 0.90$ and 0.95, and the dotted line for $w = 0.85$ (pure glycerol data were excluded from this plot). The inset shows the SE ratio for the self diffusion of glycerol (symbols as in Figure 2), where the dashed, dotted and solid lines correspond to the best fits of the data from Ref. 19, 30, and 31, respectively.

Also plotted in Figure 3 is the SE plot ($D\eta/T$ *vs.* T/T_g) for the diffusion of glycerol in supercooled glycerol-water mixtures, with the diffusion data reported by Chen *et al.*,[19] and the viscosity of the glycerol-water mixtures calculated using the procedure described previously. Glycerol diffusion coefficients in the pure solvent were not included in this figure, considering the high dispersion in the published data and that diffusion measurements were not performed for ferrocene methanol in pure glycerol.

Above the decoupling temperature, the radius of glycerol is 0.20 ± 0.03 nm, calculated from Eqn. (1), which is smaller than that of ferrocene methanol. This value was calculated from the constant values of $D\eta/T$ for the mixtures with $w = 0.90$ and $w = 0.95$, because for the mixture with $w = 0.85$ it is observed (see Figure 3) that the ratio $D\eta/T$ is not strictly constant.

Within the experimental error of the diffusion measurements, it is observed that the SE plot for the diffusion of glycerol in its aqueous mixtures, with the recalculated values of viscosity of the glycerol-water mixtures, exhibits a pattern similar to that reported in this work for ferrocene methanol, the decoupling reduced temperature does not depend on the solution composition. The decoupling reduced temperature observed in Figure 3 for glycerol in its aqueous solutions is 1.50 ± 0.01, for all the studied mixtures with concentrations in the range $w = 0.85 - 0.95$, similar to the decoupling reduced temperature observed for ferrocene methanol in these mixtures at $T/T_g = 1.53 \pm 0.02$. On the contrary, Chen *et al.*[19] claimed that the decoupling reduced temperature for the diffusion of glycerol increases systematically from 1.50 to 1.63 when the glycerol concentration increases from $w = 0.85$ to $w = 1$. This trend is not observed either for glycerol diffusion data or for the diffusion coefficients of ferrocene methanol using a viscosity fit that includes an extended viscosity data base.[26]

It is important to stress that the differences found between the SE product reported in Figure 3

for the diffusion of glycerol and that reported by Chen et al.[19] can be mainly attributed to

differences in the calculated viscosities. Chen et al. calculated the viscosities of the aqueous

mixtures in the supercooled region extrapolating data from the stable liquid regime, while in this

work we calculated the viscosities in this region using the Avramov-Milchev model,[27,28] with

parameters determined using experimental data including the supercooled regime.[26] On the other

hand, as mentioned previously, the calculation of T_g for the glycerol-water mixtures using an

empirical formula[19] or the Gordon-Taylor equation, only shift the reduced temperature in minor

proportion, and do not alter the decoupling pattern displayed in Figure 3.

It is well known that a fractional SE relation:

$$\frac{D\eta^{\alpha}}{T} = cte. \tag{6}$$

with a decoupling parameter $\alpha < 1$, can be used to describe the self-diffusion or the diffusion of

probes below the decoupling temperature and close to T_g.[33] From Figure 3, from the slope in the

decoupling region we obtain $\alpha = 0.8 \pm 0.1$ for ferrocene-methanol and $\alpha = 0.83 \pm 0.01$ for

glycerol (excluding pure glycerol data). The similarity in the α values was expected considering

that previous experimental[33,34] and theoretical studies[35] indicate that, in a single component

supercooled system, α is similar for probes comparable in size, and it decreases (stronger

decoupling) with decreasing probe size.

One can speculate that probe-solvent interactions could have an influence on the magnitude of

the decoupling, mainly in binary mixtures where preferential interactions with one of the

components can occur, leading to a modification of the environment of the diffusing probe. To validate this assumption we can compare the obtained decoupling parameters with that obtained for ferrocene methanol in aqueous sucrose ($\alpha = 0.65 \pm 0.06$), and for fluorescein disodium salt in aqueous trehalose ($\alpha = 0.42 \pm 0.08$). Considering that these probes have similar sizes, we believe that the stronger decoupling observed for the fluorescein salt could be due to its ionic character, in spite of the different nature of the supercooled mixture. If the proposed correlation between interaction and decoupling is accepted, similar decoupling parameters for ferrocene methanol and glycerol in supercooled glycerol solutions would imply similar hydrogen-bonding interactions with the mixture components.

The SE plots for the self-diffusion of glycerol, shown in the inset of Figure 3, exhibit a completely different behavior depending of the data source. Thus, $D\eta/T$ calculated with the data from Kruk et al.[31], seems to indicate a decoupling at $T/T_g \approx 1.45$, similar to that observed for ferrocene methanol and glycerol in glycerol-water mixtures. A qualitatively similar behavior is observed for $D\eta/T$ calculated from the data by Chang and Sillescu,[30] up to $T/T_g \approx 1.7$. However, an unusual increase of the SE ratio is observed with increasing reduced temperature, instead of the constant value expected if the SE relationship holds. Even more tricky is the behavior of $D\eta/T$ calculated from data by Chen et al..[19] Although the expected constant behavior is observed at high reduced temperatures down to $T/T_g \approx 1.35$, a decoupling in the opposite direction is observed at lower T/T_g, that is the diffusion coefficient decrease more rapidly than the viscosity increase with decreasing temperature. As it was already pointed out, the diffusion coefficients reported by Chen et al.[19] at the three lowest temperatures (Figure 2) clearly deviate from the general tendency, and a systematic error in the diffusion measurements in that low temperature region could be responsible for the anomalous behavior.

In summary, at the light of the reported results, the temperature dependence of the SE product for the self diffusion coefficient of glycerol is controversial and new and more reliable results in the supercooled region are needed to prove that the behavior observed for glycerol-water mixtures is also applicable for pure glycerol. However, it is reasonable to assume that the behavior exhibited by glycerol in glycerol-water mixtures that approach pure glycerol should be similar to that in pure glycerol, as supported by the glycerol self diffusion data reported by Kruk *et al.*[31]

Finally, it is worth to note that our conclusions of the independence on composition of the decoupling reduced temperature for the translational diffusion of ferrocene methanol and glycerol in aqueous glycerol solutions are validated by results for the rotational correlation time (τ_r) of the probe TEMPO (2,2,6,6tetramethyl –1-piperidine-1 oxi), determined by ESR,[36] in glycerol aqueous solutions with glycerol mass fractions in the range $0.23 < w < 0.965$.

The rotational equivalent to the SE relation is the Debye-Stokes-Einstein (DSE) relation,[37]

$$\frac{1}{\tau_r} = \frac{3k_B T}{4\pi\eta\, r^3}$$ (7)

which relates τ_r (or the inverse of the rotational diffusion coefficient, D_r) with the viscosity of the solvent and the size of the probe, with radius r.

As it can be observed in Figure 5, for $w > 0.8$ the DSE ratio, $\eta/\tau_r T$, is not constant, meaning that there is a decoupling between the rotational and the structural relaxation times. However, the magnitude of the decoupling is independent of the solution composition, as observed for the translational diffusion of ferrocene methanol and glycerol. Below $w < 0.8$ it is observed that

$\eta/\tau_r T$ becomes dependent of the composition, probably as a consequence of a change in the mesoscopic structure of the mixture.

In fact, a liquid-liquid transition (LLT) has been found for water-rich mixtures,[38] although the influence of this LLT on the dynamic properties of the mixtures has not been analyzed yet.
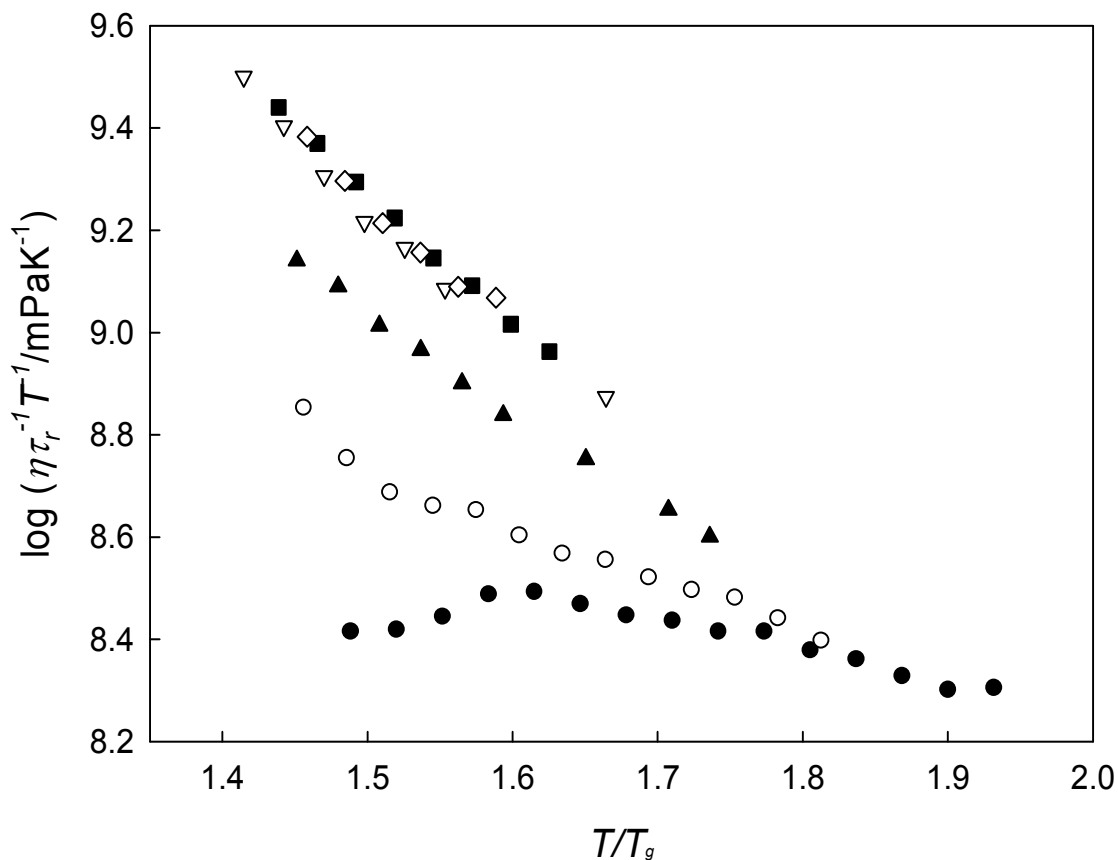

Figure 5: Debye-Stokes-Einstein ratio as a function of the reduced temperature for TEMPO (2,2,6,6 tetramethyl –1-piperidine-1 oxi) in glycerol-water mixtures for ($\bullet$) $w = 0.454$, ($\circ$) $w = 0.654$, ($\blacktriangle$) $w = 0.770$, ($\triangledown$) $w = 0.831$, ($\blacksquare$) $w = 0.919$, ($\diamond$) $w = 0.965$.[36]

The decoupling between τ_r and η for this probe occurs at a higher reduced temperature than that observed for the translational diffusion of ferrocene methanol or glycerol. This is an unexpected

result for the decoupling of the translational and rotational dynamics of a probe in a supercooled liquid,[9] but it should be considered that we are comparing different probes, ferrocene methanol and TEMPO, in a supercooled binary mixture where specific interactions of the probes with the mixture components could dominate the dynamics. Moreover, recent simulations[39,40] have emphasized the inadequacy of the Debye model, implicit in the ESR data used in this analysis, to describe the correlation between translational and rotational dynamics.[40]

4. CONCLUSIONS

The diffusion of ferrocene methanol in supercooled glycerol-water mixtures was measured using a chronoamperometric technique on disk and cylindrical microelectrodes. By changing temperature and composition, we measured the diffusion coefficient of the probe covering almost five orders of magnitude in the viscosity, allowing the analysis of the validity of the Stokes-Einstein relation as a function of composition. Diffusion-viscosity decoupling was observed for reduced temperatures below $T/T_g = 1.53 \pm 0.02$, and it seems that the observed behavior follows a common trend for all studied compositions (mass fractions between 0.7 and 0.9). This result differs from that reported previously for the decoupling in glycerol aqueous solutions[19], where the reduced temperature for the decoupling of the glycerol diffusion seems to decrease with increasing water content. A comprehensive analysis of the viscosity of the glycerol-water mixtures in the supercooled region allowed us to conclude that the discrepancies are only apparent. When properly extrapolated values for the viscosity of the mixtures in the supercooled region are used, the breakdown of the Stokes-Einstein relation in this system is also found to be independent of the composition of the glycerol-water mixture.

Results for the rotational correlation time of TEMPO in aqueous glycerol, reported in the literature, also support our conclusions.

Thus, the results of this work for aqueous glycerol, along with the previous ones for aqueous saccharides[13-16] permit to conclude that the decoupling in supercooled polyol aqueous solutions is independent of the water content in the polyol-rich region. From the practical point of view, this feature has important implications in cryopreservation, where these supercooled solutions are widely used.

ACKNOWLEDGMENTS

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